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REVIEW

Superhydrophobic Coatings on Cellulose-Based Materials: Fabrication, Properties, and Applications

Hannu Teisala,* Mikko Tuominen, and Jurkka Kuusipalo

Wettability of a solid surface by a liquid plays an important role in several phenomena and applications, for example in adhesion, printing, and self-cleaning. In particular, wetting of rough surfaces has attracted great scientific interest in recent decades. Superhydrophobic surfaces, which possess extraordinary water repelling properties due to their low surface energy and specific nanometer- and micrometer-scale roughness, are of particular interest due to the great variety of potential applications ranging from self-cleaning surfaces to microfluidic devices. In recent years, the potential of superhydrophobic cellulose-based materials in the function of smart devices and functional clothing has been recognized, and in the past few years cellulose-based materials have established themselves among the most frequently used substrates for superhydrophobic coatings. In this Review, over 40 different approaches to fabricate superhydrophobic coatings on cellulose-based materials are discussed in detail. In addition to the anti-wetting properties of the coatings, particular attention is paid to coating durability and other incorporated functionalities such as gas permeability, transparency, UV-shielding, photoactivity, and self-healing properties. Potential applications for the superhydrophobic cellulose-based materials range from water- and stain-repellent, self-cleaning and breathable clothing to cheap and disposable lab-on-a-chip devices made from renewable sources with reduced material consumption.

1. Introduction

Various techniques based on plasma deposition,[1] chemical vapor deposition (CVD),[2] atomic layer deposition (ALD),[3] nanoparticle deposition,[4] and sol-gels[5] among others, have been introduced to create nanoscale coatings that can improve material properties and bring functionality for surfaces. One of the important material properties is wettability of a solid surface by a liquid. Surface wetting is a relevant characteristic for various materials, including cellulose-based materials such as paper, board, and cotton fabrics, as it plays an important role in the field of printing, coating, and adhesion among others. In addition to creation of a new coating layer onto a material surface, wettability and other properties of the material can

be affected by surface activation methods such as flame, corona, and plasma treatments. However, the effect of activation methods on surface wetting is typically not a permanent characteristic.[6]

In addition to the many industrial applications, wetting of solid surfaces is closely related to our daily life. For example, detergents are needed to lower the surface tension of water and thus to enable its penetration below the dirt, or rain droplets on a window may hinder the view. Surface wetting also plays an important role in the function of waterproof breathable clothing, or in phenomena such as fogging and icing of windows, windscreens, eyeglasses, and metal surfaces among others. Evidently, the ability to control the wettability of solid surfaces is of high interest.

1.1. Smooth Surfaces

Chemistry of a solid surface determines whether the surface has a tendency to repel or get wetted by a liquid. Wetting of ideal, chemically homogeneous and smooth, surface can be evaluated by the Young equation:[7]

$$\cos \theta_Y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{1}$$

where θ_Y is the contact angle (CA) of the liquid on the solid surface, and γ_{SV}, γ_{SL}, and γ_{LV} are the interfacial tensions between the solid and vapor, solid and liquid, and liquid and vapor, respectively (**Figure 1**).

In the case that water droplet CA on a surface is <90°, i.e., water has a tendency to spread over the surface, the surface is termed hydrophilic. In contrast, if water CA is >90°, and the surface thus repels spreading of water, the surface is termed hydrophobic.

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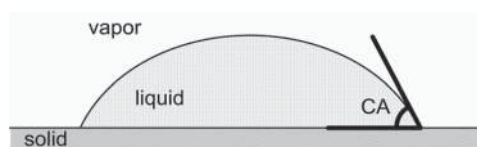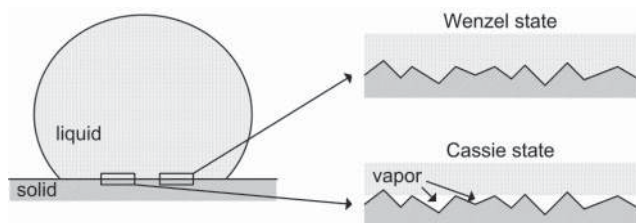E-mail: hannu.teisala@tut.fi

Figure 1. Determination of CA on solid surface.

Figure 2. Illustration of the Wenzel and Cassie wetting states on rough surface.

1.2. Rough Surfaces

Real surfaces are rarely completely smooth. Even though a surface may appear macroscopically smooth, there typically exists micro-, nano-, and molecular-scale roughness. Wetting of rough surfaces has attracted appreciable attention ever since Wenzel[8] and Cassie and Baxter[9] introduced their wetting theories for rough surfaces. Wenzel and Cassie and Baxter describe two opposite wetting states (**Figure 2**), i.e., the state where the surface is completely wetted by a liquid (Wenzel state) and the state where air gets entrapped in the roughness of the substrate and only top areas of the surface are wetted (Cassie state). Wenzel and Cassie–Baxter wetting theories are still very useful in modeling and perceiving wetting phenomena on rough surfaces. The Wenzel equation describes complete wetting state on a rough surface and is written as:

$$\cos\theta_W = r\cos\theta_Y \tag{2}$$

where θ_W is the Wenzel's CA on the rough surface, r is the actual area divided by the projected area of the surface, and θ_Y is the Young's CA on the smooth surface of the same material. Partial wetting of a rough surface can be evaluated by the Cassie–Baxter equation:

$$\cos\theta_{CB} = r_f f\cos\theta_Y + f - 1 \tag{3}$$

where θ_{CB} is the Cassie–Baxter CA on the rough surface, r_f is the actual wetted area divided by the projected wetted area of the surface, and f is the fraction of the projected area of the surface that is wetted by the liquid.

Roughness of a solid surface can enhance the surface wettability or repellency against liquid, depending on the chemical composition of the surface and the properties of the liquid. The effect of roughness on wetting of a solid surface is well illustrated by the Kao experiment.[10,11] Onda et al.[10] from the Kao Corporation executed CA measurements on rough and smooth surfaces of the same material using liquids that vary in surface tension: from the curvature of the graph shown in **Figure 3** it is easy to see that roughness of the solid has a drastic effect on wetting both in wettable ($\cos\theta > 0$) and repellent ($\cos\theta < 0$) domains.

In the case that water CA on a hydrophilic surface is <10°, and thus water spreads almost perfectly over the solid, the surface is often termed superhydrophilic. In the opposite situation, if water CA on a hydrophobic surface is >150°, and the droplet thus takes a spherical shape on the solid, the surface is often termed superhydrophobic. Other terminology that is used to

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describe superhydrophobicity include absolutely hydrophobic, ultrahydrophobic, and highly hydrophobic.[12,13] Water CA on smooth solids cannot exceed approximately 120°, which is thus the limit for chemical hydrophobicity. Therefore, superhydrophobic solids always possess appropriate surface roughness at micrometer scale and below to obtain CAs greater than 150°.

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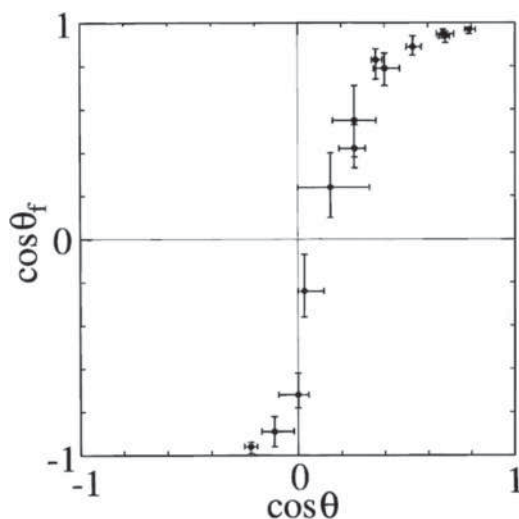
Figure 3. CA on rough surface (θ_f) as a function of CA on smooth surface (θ) of the same material. Cosine θ_f and cosine θ >0 correspond to wettable domains (CA < 90°), while cosine θ_f and cosine θ <0 correspond to repellent domains (CA > 90°). Reproduced with permission.[10] Copyright 1996, American Chemical Society.

Superhydrophobic surfaces, which possess extraordinary water repellency properties due to their low surface energy chemistry and specific nano- and microscale roughness, are of particular interest due to the great variety of potential applications ranging from self-cleaning surfaces to microfluidic devices. Another driving force for the extensive scientific work on superhydrophobicity has been a desire for detailed understanding of wetting phenomena on different types of superhydrophobic surfaces, for example on natural superhydrophobic surfaces of lotus leaves where easy mobility of water droplets results in self-cleaning effect, or rose petals where water droplets firmly adhere to the surface. The considerable scientific interest which superhydrophobic surfaces have attracted in the past decade becomes evident in the extensive amount of original research carried out in the field but also in the numerous books and review articles which take a general view on surface wetting and superhydrophobicity,[14–17] or focus on some specific topics such as characterization of plant surfaces,[18] biomimicking,[19,20] and applications of bio-inspired surfaces.[21] Another relevant topical reviews on superhydrophobicity focus on biomedical applications,[22] wettability switching,[23] durability and self-healing functions,[24] and progress in fabrication of the surfaces.[12,25] In addition to the extensive experimental research, many theoretical studies have been executed on superhydrophobicity, e.g., related to the transitions between the Cassie and Wenzel wetting states.[26,27]

Although the research in the field of superhydrophobicity has been particularly active in recent years, the extreme water repellency of some natural surfaces, e.g., duck feathers, have been recognized for much longer. The artificial fabrication of surfaces with the extreme water repellency has a long tradition as well.[28] For example, already in 1944 Cassie and Baxter[9] biomimicked the structure of duck's feathers by wounding wires parallel to one another. After coating the wire surface with a thin film of paraffin wax, they achieved extremely

water-repellent surface on which advancing water CA greater than 150° was measured. Cassie and Baxter also highlighted the easy mobility of water droplets on such porous surfaces, and stated its importance in function of waterproof clothing to enable rain drops readily roll off the clothes without wetting the surface. Another example of the fundamental work on water repellency on porous surfaces is the waterproof and breathable GORE-TEX fabrics, where the porous functional layer in the fabric, a stretched poly(tetrafluoroethylene) (PTFE) film, was patented already in 1970s.[29] In a later study, Zhang et al.[30] demonstrated how water CA on a PTFE film surface increased from 118° to 165° due to extension of the film and the related increment of fraction of air between the PTFE crystals on the porous surface.
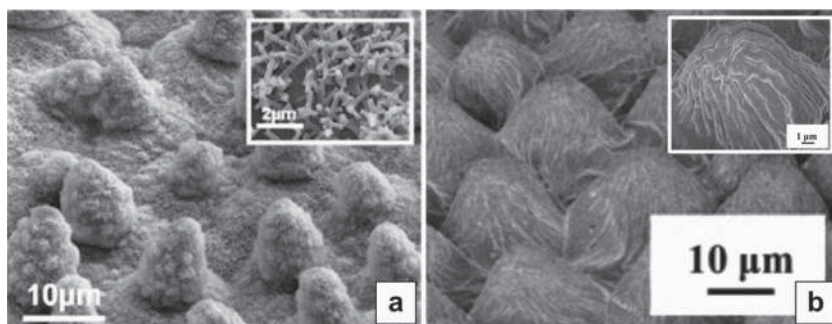
In the past few years, the great potential of superhydrophobic cellulose-based materials in the function of smart devices and functional clothing has been recognized, and cellulose-based materials such as cotton, paper, and board have established themselves among the most frequently used substrates for superhydrophobic coatings. To date, over 40 different approaches to fabricate superhydrophobic coatings on cotton and paper have been reported. This article gathers the research together, and provides an extensive review on fabrication of the superhydrophobic coatings on cellulose-based materials, the coating properties, and their potential applications.

2. Characterization of Superhydrophobic Surfaces

Although superhydrophobic surfaces have in common the high static and high advancing water CA, the receding CA and droplet adhesion can vary a lot depending on the chemical and physical nature of the surface. Therefore, in addition to the static CA, contact angle hysteresis (CAH) and sliding angle (SA) are commonly used to characterize anti-wetting properties of superhydrophobic surfaces. CAH is determined as the difference between advancing and receding contact angles of a droplet, whereas SA is the tilt angle of the substrate at which the droplet starts to slide or roll off the surface. Low CAH and SA on a superhydrophobic surface indicate that water does not penetrate into the surface roughness at large extent, but water droplets sit on the asperities of the surface with small liquid-solid contact area and low adhesion, i.e., the droplets reside in the Cassie state. In contrast, large CAH and SA indicate that water has, at least partially, penetrated into the roughness of the surface, and thus the droplet resides in the Wenzel state. In such case, droplet can adhere tightly to the surface due to the large liquid-solid contact area, where the electrostatic forces such as van der Waals interactions govern the high droplet adhesion.

Measuring of CAH, however, can be challenging. This was recently pointed out by Korhonen et al.,[31] who demonstrated that reliable determination of the receding CA may require surprisingly large initial droplet volume. At the moment, there are not any generally accepted procedures to execute the CAH or SA measurements, but the used methods and droplet volumes vary a lot. Therefore, it is important to bear in mind that direct comparison between different studies and surfaces is not valid if the experimental procedures vary from one to the other,

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Figure 4. Scanning electron microscope (SEM) images of hierarchically structured functional superhydrophobic surfaces of (a) lotus leaf (Reproduced with permission.[18] Copyright 2009, Elsevier) and (b) rose petal (Reproduced with permission.[35] Copyright 2008, American Chemical Society). Insets show the wax tubules and cuticular folding on the epidermal cells of the lotus and rose surfaces, respectively.

because the experimental differences between the studies can result in great differences in the observed CAH and SA results.

Many scientists have proposed that in addition to the static CA greater than 150°, another criterion for superhydrophobicity should be low CAH or low SA. On the other hand, it is commonly accepted that superhydrophobic surfaces can create high adhesion to water droplets. In such cases, the words "sticky"[12,13,32] or "high-adhesion"[33–35] are typically used to describe the high-adhesive nature of the superhydrophobic surfaces. To clarify the used terminology in the field, Marmur et al.[36] proposed a three-layer methodology to be used with hydrophobic surfaces, according which superhydrophobic solid surfaces, which do not have a very low CAH, should be termed as parahydrophobic surfaces. In this Review, we consider the static CA greater than 150° as a sole criterion for superhydrophobicity, and CAH and SA values are reported to emphasize differences in the anti-wetting properties between the surfaces.

Throughout history, humans have learned from nature. There are several natural examples of different types of superhydrophobic surfaces on plants, insects, and animals.[18–20,37] Self-cleaning of lotus leaves (**Figure 4**a),[18,38] high water adhesion on rose petals (Figure 4b),[35,39] and the ability of water striders to walk on water[40] are just few examples of functional superhydrophobicity that can be found from nature. The most famous example of superhydrophobic surface is the lotus leaf (*Nelumbo nucifera*). The dual-scale roughness of the waxy surface of lotus leaf (Figure 4a) is the basis for its superhydrophobic character with an extremely low water adhesion. Water CAs greater than 160° and CAH and SA less than 5° have been reported on lotus surface.[18,19,38] That is, water droplets reside in the Cassie state on the lotus surface, and the easy mobility of the droplets is because of the small contact area between the droplets and solid surface. Rolling droplets, for example rain water, can easily collect contaminating particles from the plant leaf keeping the surface clean. The self-cleaning effect, also referred to as the lotus-effect, has been demonstrated on various superhydrophobic plant leaves by Barthlott and Neinhuis,[38,41] who firstly reported on the self-cleaning effect of lotus leaves as well. The self-cleaning ability biomimicked from the natural surfaces is among the most frequently suggested functions of artificial superhydrophobic surfaces.

Another type of superhydrophobicity takes place on petals of many roses (Figure 4b). The superhydrophobic rose petals can create high adhesion to water droplets. The high-adhesive superhydrophobicity on red rose petal (*rosea Rehd*) was firstly characterized by Feng et al.,[35] who reported that water droplets as large as 10 µL were able to remain on the petal surface when tilted upside down. The round and grooved hierarchical roughness of the high-adhesive superhydrophobic rose petals, completely different from the tubular structure of lotus leaves, contributes to combined wetting of the surface between the Wenzel and Cassie states, which enables large liquid-solid contact area and high water droplet adhesion.[39]

3. Artificial Superhydrophobic Surfaces

3.1. Fabrication

A great variety of methods to fabricate superhydrophobic surfaces on different substrates have been introduced in recent years. A typical approach to create a superhydrophobic surface is either to pattern a hydrophilic material and coat the surface afterwards with a thin layer of hydrophobic material, or to pattern some inherently hydrophobic material. Low surface energy materials such as siloxanes or fluoropolymers are typically used to obtain the hydrophobic chemistry on artificial superhydrophobic surfaces. However, the extremely low energy surface chemistry is not a necessary condition for superhydrophobicity, because natural superhydrophobic surfaces, which can have extremely high CAs and low SAs, possess only moderately low energy chemistry on their waxy surface.

Almost any solid material, e.g., hard solids such as metals and metal oxides, elastic and flexible polymers, and fiber-based materials such as paper and textiles, can be used as a substrate for a superhydrophobic surface. Among others, plasma, laser, and chemical etching can be used to roughen solid substrates in order to fabricate a superhydrophobic surface. Photolithography is a common way to create well-defined silicon micropillar arrays for superhydrophobic surfaces. Other frequently used methods to fabricate superhydrophobic surfaces include the use of different templates, electrospinning of nanofibers, evaporation of polymer solutions, sol-gel coatings, and various spraying techniques e.g., using nanoparticle suspensions.[12,15] In fact, a superhydrophobic coating can be fabricated as easily as by collecting candle soot on a glass slide or metal surface.

3.2. Applications

Superhydrophobic surfaces and coatings can potentially be utilized in variety of applications including self-cleaning, stain-resistant, anti-icing, and anti-fogging surfaces; wind screens; waterproof breathable clothing and coatings; anti-biofouling

and anti-corrosion coatings; fog-harvesting; oil separation from water; microfluidics; drag reduction; and liquid transportation. In addition to the special wettability, many other useful properties have been typically incorporated into superhydrophobic coatings, for example transparency, structural color, gas permeability, and flexibility.[12,15,17]

Wettability alteration on superhydrophobic surfaces has attracted great scientific interest due to its many potential applications, e.g., in the field of microfluidic devices. Surface roughness can support either hydrophobicity or hydrophilicity depending on the surface chemistry, and therefore, it is easy to execute a superhydrophobicity-superhydrophilicity conversion on a textured surface simply by changing its chemistry. Various external stimuli, including electric-field, heating and cooling, extension, solvent treatments, plasma treatments, self-assembly, and illumination, can be used to realize the wettability conversion on different types of superhydrophobic surfaces. Typically, the wettability switching can be done repeatedly using one stimuli to induce the hydrophilicity conversion and another to return the hydrophobicity.[16,23] Photo-induced wettability changes on photoactive inorganic materials such as titanium dioxide (TiO_2) and zinc oxide (ZnO) have been of particular interest in recent years both because of their potential practical applications and the lack of fundamental understanding of the phenomena.[42,43] Benefit of the photocatalytic wettability switching is that it enables the control of surface properties with high level of details. By illuminating the sample through a photomask, micrometer scale surface energy patterns can be fabricated on, for example, TiO_2 to control its surface wettability. Zhang et al.[44] demonstrated fabrication of 50 µm wide superhydrophilic stripes on a superhydrophobic octadecylphosphonic acid (ODP) -modified TiO_2 surface, which were able to guide water condensation (**Figure 5**a,b) and deposition of polystyrene (PS) microspheres from aqueous suspension. Teisala et al.[43] demonstrated surface energy patterning and selective adsorption of colored water on photopatterned superhydrophobic TiO_2 nanoparticle coated paper (Figure 5c,d). Sirringhaus et al.[45] demonstrated how surface energy patterning could be used in the field of printed electronics to control deposition of conductive ink droplets in fabrication of integrated circuits.

Because of the high surface tension of water (72.1 mN/m), fabrication of superhydrophobic surfaces is relatively easy. Natural superhydrophobic surfaces have shown that extremely low surface energy materials are not needed to obtain high CA, low SA, and low CAH for water. Neither are the requirements for the physical structure of the surface especially strict, but superhydrophobicity can be obtained, for example, on simple micropillar surfaces. When the target is to achieve repellency against liquids of significantly lower surface tension than water, requirements for both the chemistry and physical structure of the surface are much stricter. For example, any fluorine-free surfaces have not been reported to possess high CAs for low
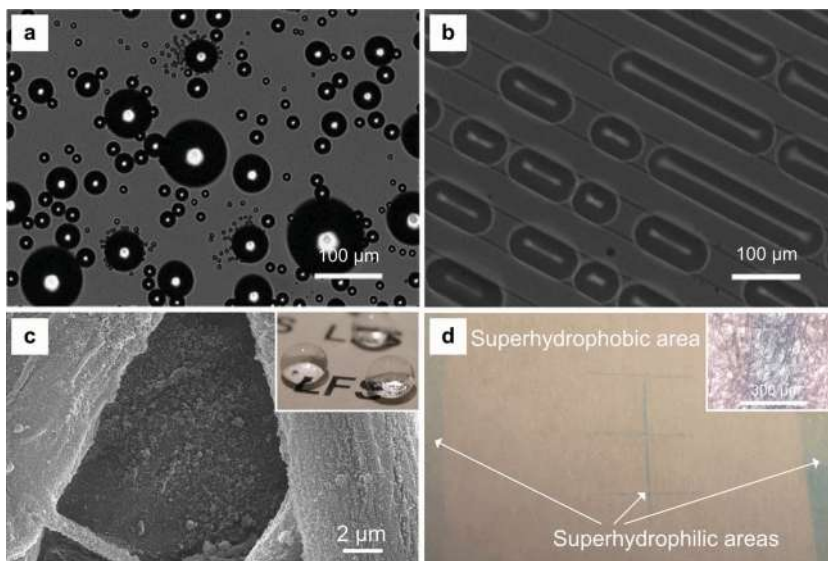

Figure 5. Wetting of photopatterned superhydrophobic TiO_2 surfaces. Optical micrographs of water condensation on ODP-modified superhydrophobic TiO_2 surface (a) before and (b) after the creation of superhydrophilic patterns by illumination. Reproduced with permission.[44] Copyright 2007, American Chemical Society. (c) SEM micrograph of superhydrophobic TiO_2 nanoparticle coating on paper (inset: photograph of water droplets on the transparent coating), and (d) methylene blue colored water rod-coated on photopatterned superhydrophobic TiO_2 nanoparticle coating on paper (inset: optical micrograph of the colored pattern). Reproduced with permission.[43] Copyright 2012, Springer.

surface tension liquids such as oils. Tuteja et al.[46,47] carried out a pioneering work on superoleophobic surfaces and demonstrated the critical role of re-entrant curvature in anti-wetting properties of fluorinated T-letter shaped or mushroom-like micropillar surfaces (**Figure 6**). In addition to water, the re-entrant curved micropillar surfaces could repel low surface tension liquids such as hexadecane (27.5 mN/m). In recent years, interest towards superamphiphobic surfaces capable of repelling both water and oils has grown increasingly, and some studies on fabrication of superamphiphobic coatings on cellulose-based materials have been reported as well.[48–50] However, because of the strict requirements for the chemistry and physical structure, superamphiphobic surfaces are rare.
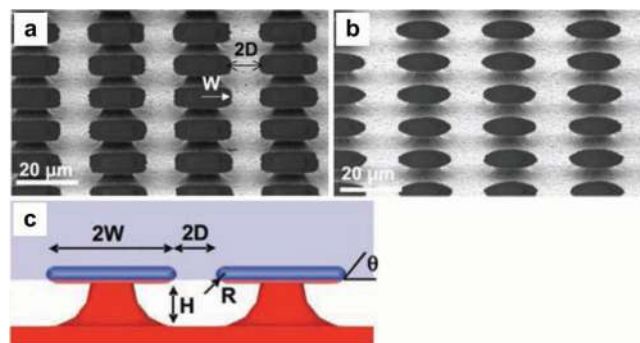
Figure 6. Superamphiphobic surfaces with re-entrant curvature. (a,b) SEM micrographs of the micropillar surfaces with re-entrant topography and (c) a cartoon highlighting the formation of a liquid-solid-air composite interface on the re-entrant curved surface. Reproduced with permission.[46] Copyright 2007, AAAS.
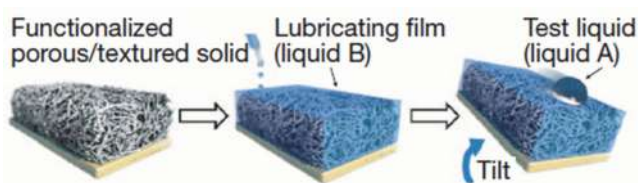
Figure 7. Principle of SLIPS. A porous/textured solid is infused by a lubricating fluid to form an extremely low-friction smooth surface. Reproduced with permission.[51] Copyright 2011, Nature Publishing Group.

Recently, Wong et al.[51] introduced a new approach to create slippery surfaces with pressure-stable omniphobicity and self-healing properties. The idea is that a porous substrate, similar to many superhydrophobic surfaces, is infused with a lubricating fluid (**Figure 7**). While the substrate resembles superhydrophobic surfaces, the strategy to create slippery surfaces using lubricating fluids is very different from superhydrophobicity, because the lubricating fluid (e.g., perfluorinated liquid), which is locked in place by a nano/microporous substrate, creates a smooth and slippery surface for both high- and low surface tension liquids. The as-prepared slippery liquid-infused porous surfaces (SLIPS) had minimal adhesion to variety of liquids, e.g., liquids with low surface tension such as hexane (18.6 mN/m). Droplets of various liquids could easily slide on the surface without leaving any stain: the measured CAH values were <2.5° and SAs were ≈5° at the maximum. Once again, inspiration for the surface design was found from nature, from the Nepenthes pitcher plants.[52] Any method to fabricate superhydrophobic coatings can potentially be used to create rough surface texture for SLIPS, because the structural details are irrelevant to the resulting performance of the surface.[51] Various potential applications have been suggested for SLIPS, for example, fluid handling in biomedical applications, fuel transport, and self-cleaning surfaces.[51,53] In case of cellulose-based superhydrophobic materials, SLIPS could potentially be utilized, for example, in food packages to ease emptying of a package and thus to reduce the amount of waste food remaining in the package. In large-scale industrial exploitation, such breakthrough applications would contribute to a global ecological impact.

Even though many promising applications for superhydrophobicity have been identified, and there are several facile methods to fabricate superhydrophobic surfaces and coatings, the large-scale utilization of superhydrophobic surfaces is limited. This is mainly due to the poor wear resistance, which is a common problem with superhydrophobic surfaces.[12,17] The fragile micrometer and submicrometer scale surface structures are easily damaged in daily use, for example, due to abrasion. Artificial superhydrophobic surfaces cannot renew and heal the damages similarly to natural surfaces. Fabrication of robust surfaces, which can maintain their functionalities also in wearing conditions, is one of the major issues to be resolved with superhydrophobic and other functional surfaces.

3.3. Durability

Durability is a fundamental challenge with superhydrophobic surfaces. However, recently there has been major progress in fabrication of robust superhydrophobic surfaces. For example, Deng et al.[54] fabricated a robust superamphiphobic coating using candle soot as a template. The coating showed CAs greater than 150° for low surface tension liquids such as hexadecane, and could maintain its liquid-repellent properties even when the topmost surface layer was worn out or peeled off using adhesive tape. Zhao et al.[55] fabricated a grooved surface with re-entrant curvature to obtain directional superamphiphobicity and mechanical robustness, and Zhou et al.[56] applied a highly durable superhydrophobic silicone rubber/nanoparticle composite coating on fabrics, which was capable of withstanding 500 laundering cycles without any significant change in its anti-wetting properties.

Recently, also self-healing functions have been successfully incorporated into superhydrophobic surfaces.[48,57,58] Apparently, the first self-healing superhydrophobic coating was introduced by Li et al.[57] Their porous micro-/nanostructured fluoro-modified polymer coating could preserve healing agent units of reacted fluoroalkylsilane, and the preserved healing agents could migrate to the coating surface to heal its chemistry after the original fluoroalkylsilane layer was decomposed by an oxygen plasma treatment. However, so far there are no artificial superhydrophobic surfaces which are capable of healing physical damages similarly to SLIPS or natural superhydrophobic surfaces.

Although many natural superhydrophobic surfaces possess a dual-scale roughness that contributes to easy mobility of water droplets and self-cleaning properties, by now it is clear that hierarchical surface roughness is not a necessary condition for superhydrophobicity with low droplet adhesion and self-cleaning properties, but similar superhydrophobic properties can be achieved with a single-scale submicrometric surface roughness. It seems reasonable that one important reason why nature has chosen dual-scale hierarchical roughness for many of its superhydrophobic surfaces, e.g., lotus leaf, is the enhanced wear resistance of the fragile surfaces.[27,59]

To date, many surprisingly durable superhydrophobic coatings, which can tolerate a multitude of laundering cycles, have been successfully fabricated on cotton and other fabrics. Many fiber-based materials are actually favorable substrates to fabricate durable superhydrophobic coatings, because the multi-scale hierarchical roughness originating from the fiber structure of the substrate can protect the coating from abrasive contact as was demonstrated by Zimmermann et al.[60] on silicone nanofilament coated poly(ethylene terephthalate) (PET) fabric (**Figure 8**): abrasion destroyed the coating only from the topmost areas of the fibers and the sample could maintain its liquid-repellent properties. Moreover, capability of soft and flexible substrate materials to yield under mechanical stress can prevent a superhydrophobic coating layer from damaging.

4. Superhydrophobic Coatings on Cellulose-Based Substrates

4.1. Cellulose as a Substrate Material

Cellulose is an abundant biopolymer, which is commonly used as a raw material for paper products and cotton fabrics.

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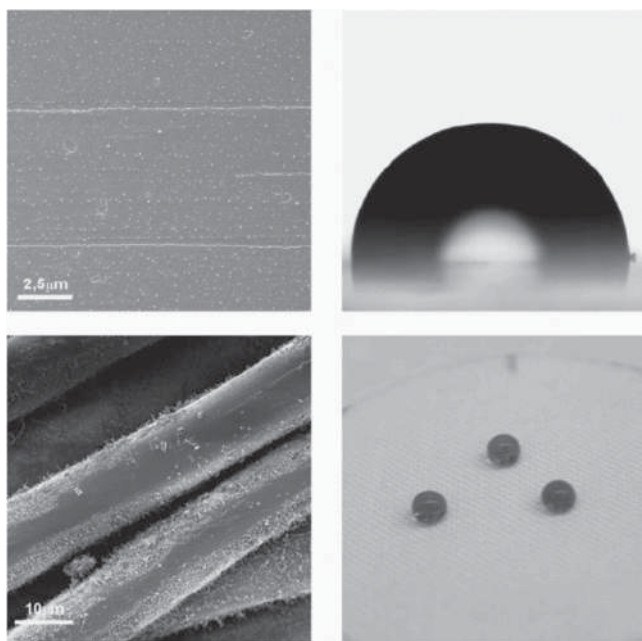
Figure 8. SEM micrographs of silicone nanofilament coated samples after abrasion test and droplets of water showing the wetting properties of the corresponding samples. Upper row: glass surface. Lower row: PET fabric. Reproduced with permission.[60]

Cellulose chemistry includes a great number of surface hydroxyl (OH) groups, which readily create hydrogen bonds with water molecules enabling water to spread over the surface. Cellulose is also capable of absorbing water. That is, cellulose is a hydrophilic and hygroscopic material by nature. Water CAs reported on smooth cellulose films vary between 17° and 47°.[61] The rough and porous surface structure of paper and cotton fabrics further enhance spreading and absorption of water by capillary action between the cellulose fibers. The capillary driven liquid transportation is utilized, for example, in paper-based microfluidic devices.[62]

In order to fabricate hydrophobic paper or cotton, sort of hydrophobization treatment needs to be carried out. Although cellulose fibers create a rough surface structure, for example on paper, typically water CAs greater than 150° are not reached on paper surface after hydrophobization treatments. Even with low surface energy fluorine coatings the CAs typically remain below 150°, and water droplets firmly adhere to the surface. For example, Mukhopadhyay et al.[63] used four types of plasmas from different fluorine-containing monomers to coat filter paper. Already, a very thin layer of fluorocoating (thickness less than 1–2 nm) turned the initially hydrophilic surface hydrophobic: CAs on the plasma coated surfaces varied between 141° and 146°. However, increment in the coating thickness did not further increase the CAs. Balu et al.[32] deposited thin fluorocarbon films on commercial copy-grade paper and hand-made sheets using plasma-enhanced chemical vapor deposition (PECVD). After the plasma coating, both surfaces showed high CAs between 140° and 145° and large CAHs between 60° and 110°.

When looking at the fiber structure of paper surface, it is not surprising that after hydrophobization treatment the surface becomes nearly superhydrophobic, but water droplets still adhere firmly to the surface, because paper surface resembles, to some extent, the high-adhesive surface of rose petals.[35,39] That is, although air gets entrapped between the cellulose fibers on a hydrophobic paper surface creating a liquid-solid-air composite interface, the round and grooved structure of the fiber surface enables large liquid-solid contact area and high adhesion of water droplets. In order to fabricate a superhydrophobic surface on paper or cotton, chemical modification alone is not enough, but in most cases the surface roughness needs to be modified as well.

Fabrication of superhydrophobic surface on cellulose-based substrates such as paper, board, and cotton fabrics has recently attracted appreciable attention of scientists. These versatile and economically viable materials, made of renewable and biodegradable cellulose fibers, have many profitable properties such as affordability, recyclability, flexibility, breathability, and mechanical strength. Superhydrophobic surface properties on paper, board, and cotton can further broaden their exploitation potential and open new possibilities, for example, in the fields of printing, diagnostics, and microfluidics. Fabrication of superhydrophobic surface on cellulose-based materials, however, can be challenging because of the complex surface structure and limited thermal and chemical resistance of the substrate material. Therefore, suitable methods to fabricate a superhydrophobic surface on paper and cotton are limited. Apparently, Lin et al.[64] carried out the first study where a superhydrophobic coating was applied on cotton in 2005 by spray-coating the substrate with TiO_2 nanoparticle containing fluoro-copolymer solution, while Nyström et al.[65] firstly reported on fabrication of superhydrophobic paper in 2006 via tailored grafting architecture. Since then, the number of research papers published on fabrication of superhydrophobic cotton or paper has exploded.

As was discussed earlier, one of the major challenges with superhydrophobic surfaces is the long-term durability and wear resistance. Indeed, durability is one of the key issues with superhydrophobic cotton clothes which need to stand abrasion and repeated washing cycles. However, the applications of paper products are typically quite different from the applications of cotton fabrics. Paper products are typically cheap and disposable, and they are produced in high volumes for short-term applications. Because of the nature of the substrate material, in case of paper it is even more important to seek new methods suitable for low-cost roll-to-roll mass production of superhydrophobic surfaces than focus on the surface durability. In the following sections, different approaches to fabricate superhydrophobic coatings on cellulose-based materials are explored and properties of the surfaces are discussed with focus on technical aspects of fabrication of the coatings, surface wettability, and coating durability.

4.2. Fabrication of Superhydrophobic Coatings on Cellulose-Based Substrates

The two general rules that superhydrophobic surfaces must fulfill apply to superhydrophobic coatings on cellulose-based

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materials as well: the coating must have an appropriate surface structure at micrometer scale and below, and the coating must have at least moderately low surface energy chemistry, e.g., from hydrocarbon or fluorine compounds. There are various approaches to satisfy the two requirements to obtain superhydrophobic properties for cellulose-based materials such as paper and cotton. The most common approaches to fabricate superhydrophobic coatings on cellulose-based materials include various dip-coating methods, spray-coating, in situ nanorod/particle growth, CVD, and plasma processing techniques.

In general, the superhydrophobic coatings on paper and cotton have in common multi-scale coating roughness, which originates from the hierarchical roughness of the fiber structure of the substrate material. As was discussed earlier, the inherent surface roughness of paper or cotton cannot typically guarantee superhydrophobic properties for the surface. Therefore, the paper or cotton substrate needs to be roughened prior to application of the low surface energy coating, or alternatively, the coating layer itself must increase roughness on the surface to achieve decent superhydrophobic properties, i.e., water CA greater than 150°. The physical structure/roughness of the coating has a vital role in the anti-wetting properties of the coated material. In addition to the static CA, topography of the coating has a critical role in water adhesion and dynamic wetting properties of the surface. The existence of layer of entrapped air, i.e., plastron layer, on the surface is vital in achieving and maintaining the superhydrophobic properties. It is well-known that the plastron layer is more stable on a submicrometer scale surface texture (often referred to as nanostructure/-roughness) than on a micrometer scale texture.[66,67] The surface topography therefore has an essential role in designing coatings with stable superhydrophobic properties for, for example, water-proof clothing capable of withstanding the local pressure caused by impacting rain droplets. The critical question still remains: what is the scale for the smallest structures on a superhydrophobic surface that can maintain the plastron layer and superhydrophobic properties. With decreasing structural dimensions on a superhydrophobic surface, there is a limit dependent on the chemistry and shape of the surface structures, after which the superhydrophobic properties will vanish.[14,33,39]

The most common fabrication methods of superhydrophobic coatings on cellulose-based materials are discussed in general manner below, and some typical characteristics of the different coating methods and coatings are presented in **Table 1**. More detailed information on different approaches to fabricate superhydrophobic coatings on cellulose-based materials is presented in Sections 4.2.1 and 4.2.2.

Dip-coating[48,56,68–77] is the most common method to fabricate a superhydrophobic coating on paper or cotton substrates. It typically requires at least three individual processing steps, which include dipping in the coating slurry, drying, and curing. Typically, the coating slurry contains organic solvent, components that increase the coating roughness, e.g., nano-/microparticles, and binding component, e.g., some polymer. In addition, the coating slurry can contain hydrophobization agents, or the hydrophobization treatment can be done separately after the dip-coating procedure. Many superhydrophobic coatings fabricated by dip-coating show surprisingly good mechanical durability due to the strong binders and hierarchical roughness of the coating.

Spray-coating methods offer a facile route to fabricate superhydrophobic coatings on cellulose-based materials with good scale-up potential. The conventional spray-coating,[64,78–82] where liquid droplets of the coating slurry are sprayed on the substrate, has many similarities with dip-coating. That is, the coating composition may be very similar, and the coating procedure typically involves several processing steps, e.g., spraying of the coating slurry, dying/curing, or possible hydrophobization treatment. Novel one-step spray-coating methods[33,43,66,83–85] do not require any separate drying/curing or hydrophobization steps, but the coating formation is based on rapid physico-chemical reactions and phase transitions from liquid/gas to solid in the aerosol phase. Evidently, the advantage of these methods is their rapid one-step nature. On the other hand, the coating durability is typically not comparable to that of the coatings fabricated by, for example, dip-coating methods.

Polymerization techniques[65,86,87] enable fabrication of superhydrophobic coatings in a sophisticated manner through closely controlled chemical reactions. Drawback of polymerization techniques is their multi-step and time-consuming nature.

In situ nanorod/particle growth in liquid[49,88–91] or gas[60,92] phase can be used to fabricate well-characterized nano-/micro structures in a controlled manner. However, although it is possible to fabricate the coating in straightforward one-step process, the nanoparticle/nanotube growth cannot be considered as an especially efficient method to fabricate superhydrophobic coatings on cellulose-based materials because the growth process is typically time-consuming.

CVD[50,93] and plasma processing[13,32,94] enable tuning of chemical and physical fine structure of the substrate by means

Table 1. Common approaches to fabricate superhydrophobic coatings on cellulose-based materials and general characterization of the different coating methods and coatings.

Method	References	Number of processing steps[a]	Nature of the procedure[b]	Coating thickness [nm]	Coating durability
Dip-coating	[48,56,68–77]	3–5	slow	>100	good/moderate
Spray-coating	[33,43,64,66,78–85]	1* or 2–3**	rapid*/slow**	>100	moderate/weak
Polymerization techniques	[65,86,87]	>5	slow	±100	good/moderate
In-situ nanorod/particle growth	[49,60,88–92]	1* or >5**	slow	±100	moderate
CVD and plasma processing	[13,32,50,93,94]	1–2	moderate/slow	≤100	moderate

[a]*Corresponds to dry methods and **corresponds to wet-chemical methods; [b]Typical time-scales for slow, moderate, and rapid procedures are ≈1 h or more, ≈1–2 min, and <1 s, respectively.

of (plasma enhanced) CVD and plasma etching. The procedure typically requires two separate steps, that is, the increment of surface roughness of the substrate by etching, and deposition of a thin hydrophobic coating on the etched substrate. In the case of extremely porous and rough substrates such as nanocellulose aerogel membranes sole CVD coating can yield the surface superhydrophobic, and thus separate roughening of the surface is not required. Plasma enhanced CVD enables moderately rapid and well-controlled deposition of thin hydrophobic coatings on material surfaces. Typical limitations of plasma processing include cost of the equipment and, especially in the case of plasma etching, the batch-type and time-consuming nature of the procedure.

4.2.1. Wet-Chemical Methods

Dip-coating: Wang et al.[69] prepared a sol solution which contained silica nanoparticles with an average size of ≈50–150 nm by co-hydrolysis and condensation of two silane precursors, tetraethyl orthosilicate (TEOS) and tridecafluorooctyl triethoxysilane. The solution could be applied on various substrates, including textiles and filter paper, by dipping, spin-coating, or spraying. Because the solution itself contained a fluorocompound, any separate hydrophobization treatment was not needed to obtain the transparent and superhydrophobic coating, on which water CAs greater than 170° and SAs lower than 7° were measured. This was apparently the first so-called one-step approach to fabricate a superhydrophobic coating on paper, i.e., any separate hydrophobic modification was not needed to bring the low surface energy chemistry for the coating. However, after application of the coating solution, two additional steps, i.e., drying at room temperature and curing for 1 h at 110 °C, were still needed to finalize the superhydrophobic coating.

Arbatan et al.[70] fabricated a superhydrophobic coating on filter paper (**Figure 9**) by dip-coating the paper samples in an aqueous suspension of precipitated calcium carbonate (PCC) pigments and cellulose nanofibers, after which the samples were dried between two sheets of blotting paper in a drum dryer at 112 °C for 18 min. After the dip-coating procedure, the samples were hydrophobized in a solution of alkyl ketene dimer (AKD) in n-heptane and cured in an oven at 105 °C for 30 min. Water CA on the coated filter paper was measured to be 160°, and 5 μL water droplets instantly rolled off the surface when placed on the sample which was inclined at 5°. The cellulose nanofibers had a critical role in the formation of the hierarchically structured coating layer as they acted as binding agents between the PCC particles and the substrate.

Gao et al.[71] fabricated superhydrophobic cotton by dip-coating the fabrics in different silica sols formed by hydrolysis and condensation of tetraethoxysilane under alkaline conditions. After coating the cotton fabric with silica sol, which
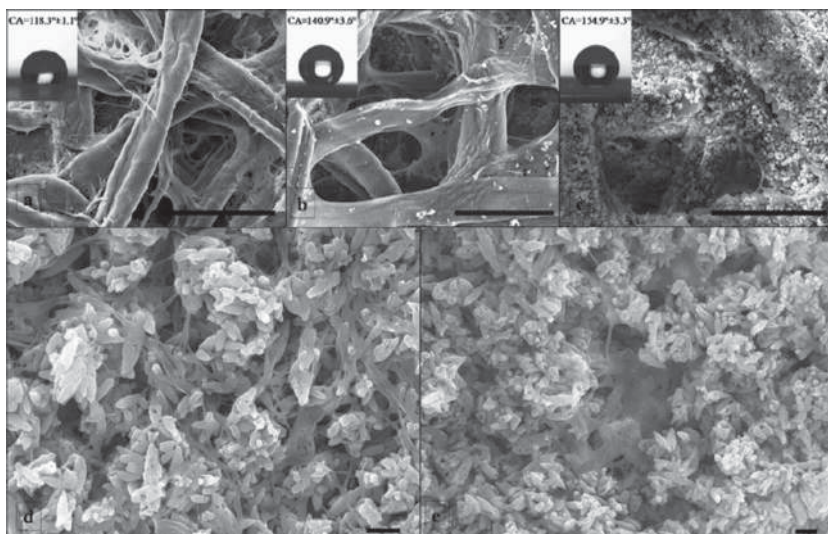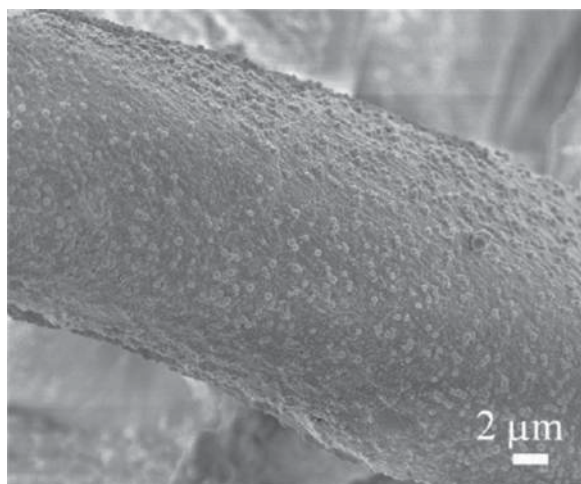

Figure 9. SEM images of PCC pigment/cellulose nanofiber coating. (a) Filter paper sized with AKD, (b) filter paper dipped in an aqueous suspension of PCC and subsequently sized with AKD, and (c) filter paper dipped in an aqueous suspension of PCC and cellulose nanofibers and subsequently sized with AKD (scale bars correspond to 50 μm). (d–e) High-magnification images of the PCC/nanofiber coating on a glass slide (scale bars correspond to 1 μm). Reproduced with permission.[70] Copyright 2012, Elsevier.

contained silica particles of ≈52 nm in diameter, the sample was padded, dried, and modified in a solution of hydrolyzed hexadecyltrimethoxysilane (HDTMS). Finally, the coating was cured at 120 °C for 1 h to obtain a superhydrophobic surface with water CA of 155°. Physical properties of the superhydrophobic cotton were compared to the properties of unmodified cotton. The comparison revealed a slight decrement in the tensile strength of the coated cotton (<10%). Changes in the whiteness and air permeability of the cotton were negligible. Laundering test revealed that the superhydrophobic coating could not withstand multiple washing cycles, because after 5 cycles water CA on the coated cotton had decreased to ≈125°, and after 30 cycles to ≈95°.

Wang et al.[72] synthesized particle-containing silica sols by co-hydrolysis and co-condensation of different silane precursors to fabricate superhydrophobic coatings on fabrics. The fabrics were dip-coated in the silica sol and padded, after which the samples were dried at room temperature and cured at 110 °C for 1 h to finish the coating. The authors highlighted that the sols could potentially be applied on the substrates with several other methods as well (e.g., by spray-coating). The effect of different sol recipes on the particle size, hydrophobicity, and durability of the coating were examined. When an epoxide group containing silane, 3-glycidoxypropyltrimethoxysilane (GPTMS), was added in the sol, hydrophobicity of the coating slightly decreased, but its laundering durability improved significantly. Water CA and SA for a 4 μL droplet on the cotton fabric coated with the GPTMS containing sol were ≈170° and <10°, respectively, and after 50 washing cycles, the corresponding values remained at ≈160° and <30°, respectively.

Zhou et al.[56] fabricated an extremely durable superhydrophobic tridecafluorooctyl triethoxysilane modified polydimethylsiloxane (PDMS)/silica nanoparticle composite coating
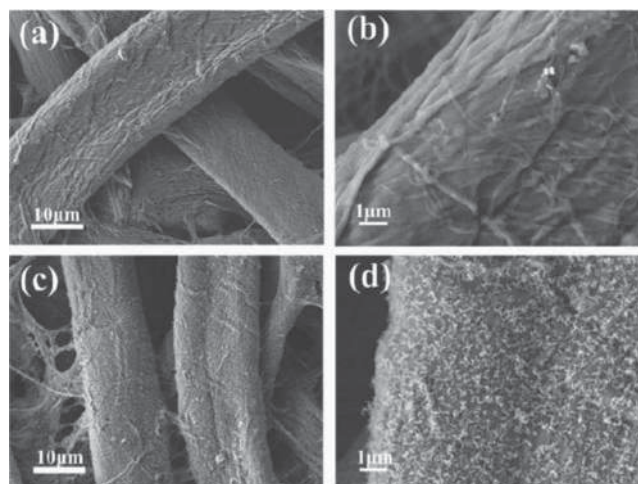
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Figure 10. SEM image of PDMS/silica nanoparticle coated cotton. Reproduced with permission.[56]

Figure 11. SEM images of filter paper surface (a,b) before and (c,d) after coating with superhydrophobic PS/silica nanoparticle layer. Reproduced with permission.[75] Copyright 2010, American Chemical Society.

to be used on different fabrics (**Figure 10**). An inspiration for the robust composite coating was obtained from tyres, a classic and highly durable nanocomposite material, where the main components are natural rubber and carbon black. The coating dispersion was applied on the fabrics by dip-coating, after which the samples were dried at room temperature and cured at 135 °C for 30 min. The authors highlighted that other coating techniques, e.g., spray-coating and padding, could be used as well. The coating showed excellent mechanical and chemical durability. For example, CA and SA for a 5 μL water droplet on pristine coated cotton were 170° and 3°, respectively, and after 500 wash cycles the corresponding values were nearly unchanged, 165° and 6°, respectively. Similar results were also obtained after treatments with boiling water and acid or base solutions. In addition to the durable superhydrophobicity, the coated fabrics showed good stain resistance and maintained their inherent good air permeability.

Duan et al.[73] treated cotton fabrics with cerium dioxide (CeO$_2$) sol using a dip-pad-cure process. The curing was carried out at 170 °C for 3 min. The whole coating procedure was repeated three times to obtain a dense film of CeO$_2$ coating on cotton. After subsequent modification of the samples in a solution of ethanol and hydrolyzed dodecafluoroheptyl-propyl-trimethoxylsilane (DFTMS), drying, and curing at 120 °C for 1 h, the cotton fabrics showed superhydrophobic properties with water CA of 158° and SA of 14° for 5 μL droplets. After 30 laundering cycles, the CA on the treated cotton still remained greater than 150°. In addition to the superhydrophobicity, the coating showed good UV-shielding properties due to the presence of aggregated CeO$_2$ nanoparticles (average size ≈15 nm).

Li et al.[74] used an industrial waterproof reagent, potassium methyl siliconate (PMS), as a starting material to fabricate superhydrophobic surfaces on paper and cotton through a simple solution-immersion method. An aqueous solution of PMS was reacted with carbon dioxide (CO$_2$) at room temperature to prepare the silanol solution, where the polymethylsilsesquioxane coatings were formed on the substrates as a result of polycondensation process and hydrogen bond interactions between

the OH-groups of cellulose molecules and silanols. To obtain a dense coating, the samples were cured in a vacuum oven at 120 °C for 30 min. Water CAs on the modified cotton and filter paper were measured to be 158° and 157°, respectively. The coating layer appeared transparent and showed satisfactory mechanical and chemical durability as the superhydrophobic character of the coated cotton textile remained after 20 washing cycles and the coating could withstand treatments with aqueous solutions over wide pH-range.

Wang et al.[75] treated filter paper with a mixture of PDMS-modified silica nanoparticles (average particle size of 14 nm) and PS solution in toluene to obtain superhydrophobic and superoleophilic filters to be used in selective absorption and separation of liquids that differ in surface tension (**Figure 11**). The treatment was carried out by dip-coating the paper in the coating solution for approximately 15 s, after which the paper was dried in an oven at 60 °C for several hours. The treated filter paper showed good superhydrophobic properties with water CA of 158° and SA of 4° for 8 μL droplets, and fully absorbed organic liquids such as diesel oil, hexane, octane, and dodecane. Chemical stability of the coating was evaluated by exposing the sample to aqueous solutions of varying pH between 1 and 14. The coating showed good tolerance to both acidic and basic conditions as the water CAs on the surface remained greater than 150°.

Bayer et al.[76] fabricated superhydrophobic cellulose sheets by dip-coating the samples in a suspension of submicrometer scale PTFE particles (≈150 nm) and ethyl-2-cyanoacrylate (ECA) monomer solution. One of the fascinating properties of ECA is that it starts cross-linking around cellulose fibers instantly after solvent evaporation due to the native OH-groups on cellulose and the moisture that has adsorbed to the surface. After dipping the cellulose sheets in the coating solution, the samples were left to dry and polymerize under ambient conditions overnight. The highest water CAs on the as-prepared surfaces were measured to be around 160°, and the coatings showed low adhesion to water droplets with CAH around 10°.

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Huang et al.[77] impregnated filter paper with fluorinated waterborne epoxy emulsion to render the paper surface superhydrophobic. The coating was cured in an IR-oven at 120 °C for 30 min. Water CA on the treated paper was 152° and the surface showed sticky properties as 5 µL droplets remained on the surface when tilted upside down. CAH on the surface was measured to be 34°. The treated paper showed potential for oil filtration from water emulsions due to its superoleophilic properties (CA for hexadecane = 0°) and good oil permeability.

Zhou et al.[48] fabricated a highly durable superamphiphobic coating with self-healing properties on polyester, wool, and cotton fabrics. The fabrics were coated via a two-step dip-coating method. In the first step, the substrate was immersed in a suspension of fluoroalkyl silane modified silica particles (average diameter ≈150 nm) in ethanol for 1 min, after which the sample was dried at room temperature for 10 min. In the second step, the sample was immersed in a fluoro-polymer/fluoroalkyl silane containing solution for 1 min and dried at 130 °C for 1 h. The coated fabrics showed great CAs and low SAs for both water and hexadecane. For example, the coated cotton showed CAs of 171° and 158° and SAs of 3° and 7° for water and hexadecane, respectively. Most of the experiments were performed using polyester fabrics as a substrate material, on which the coating could withstand at least 600 laundry cycles and several thousands of abrasion cycles without apparent change in its wetting properties. That is, both water and hexadecane CA and SA remained >150° and <10°, respectively, after the durability experiments. In addition, the coating was stable to strong acid/base, boiling, and ozone treatments, and showed very little influence on the air permeability of the fabrics. After the coating chemistry was artificially damaged by oxidizing the surface with a vacuum plasma treatment, the coating lost its super liquid-repellent properties and showed CAs of 0° for both water and hexadecane. However, the superamphiphobic properties of the coating were healed by ageing the plasma treated sample at room temperature for several hours or by a 5 min heat treatment at 130 °C. Durable superamphiphobic properties with self-healing capability, which were demonstrated using polyester fabric as a substrate material, were reported also on the coated wool and cotton fabrics.

Spray-Coating: Lin et al.[64] fabricated superhydrophobic TiO₂ nanoparticle containing fluoromethylic copolymer coatings on different substrates by spray-coating. They sprayed solution of nanoparticles mixed with perfluoroalkyl methacrylic copolymer and distilled water on the substrates by a specific nozzle and dried the coating in an oven at 85 °C for 12 h. Different coating parameter combinations were examined using cement plates as a substrate material, and the effects of different parameters were evaluated statistically by the analysis of variance and Taguchi methodologies. The solid ratio of nanoparticles in the precursor solution was concluded to be the most important single factor in preparation of the superhydrophobic coatings. The optimal parameter combination, which contained 3 layers of the coating on the substrate, resulted in oleophobic and superhydrophobic properties of the coating with water CA of 161°. The authors demonstrated fabrication of the superhydrophobic
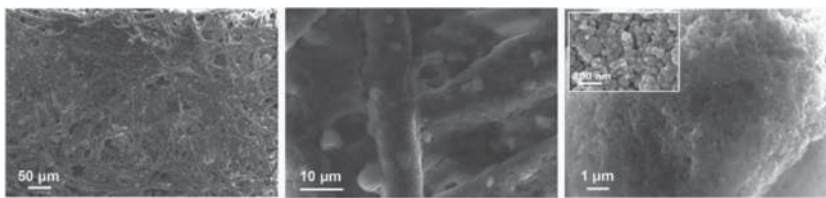
Figure 12. SEM images of different magnifications of spray-deposited SiO₂ nanoparticle coating on paper. Reproduced with permission.[79] Copyright 2012, American Chemical Society.

coating also on cotton fabric using the determined optimal parameter settings.

Bayer et al.[78] spray-coated paper and fabrics with an emulsion of surface functionalized silver flakes and colloidal copolymer blend. The first component of the blend, vinyl copolymer, was used to enable good dispersion of the silver flakes in the emulsion and to obtain good adhesion to different substrates, while the other, perfluoroethylacrylate/n-alkyl acrylate copolymer, was used to induce hydrophobic chemistry for the composite coating. Prior to the spray-deposition of the coating, a paraffin wax-based film was melted on the substrates. The spray-coating was carried out while the wax-based film was still molten at 60 °C to ensure mechanical interlocking between the coating and the melt. After 15 min of thermosetting, the coating was cooled down to room temperature. Water CA on the superhydrophobic coating was measured to be 164°, and both SA and CAH were around 5°. The coating showed good thermal stability as the SA and CAH remained below 10° after the coated paper was exposed to 80 °C for 15 h in an oven.

Ogihara et al.[79] demonstrated a simple spray-coating method to fabricate transparent superhydrophobic coating on paper and cotton (**Figure 12**). Dodecyltrichlorosilane modified silicon dioxide (SiO₂) nanoparticles (average size 25 nm) in different alcohol suspensions were manually sprayed over the substrates, after which the samples were dried at room temperature overnight. Aggregation state of the particles, and thus hydrophobicity of the coating, could be controlled by the choice of the alcohol in the nanoparticle suspension. Ethanol suspension gave the best hydrophobicity of the coating with water CA of 155° and SA of 7° for 3 µL droplets. Robustness of the coating was tested by pressing the surface with a bare finger, after which the CA and SA were measured to be 153° and 10°, respectively. The authors reported that superhydrophobicity of the coated paper was also maintained after folding the sample.

Mertaniemi et al.[80] used spray-dried nanofibrillated cellulose microparticles to fabricate a lotus-like hierarchically structured superhydrophobic surface (**Figure 13**). The dispersion of cellulose microparticles in ethanol was sprayed on a glass surface and dried in ambient conditions to form a semi-transparent coating. Hydrophobic chemistry for the coating was achieved by fluoro-modifying the cellulose microparticles with (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (FOTS). Two types of approaches were used in the surface modification: in the first approach the modification was accomplished after the spray-coating by CVD at 90 °C for 8 h, and in the second approach the modification was carried out prior to the spray-coating in toluene dispersion. In both cases, the coating appeared as low-adhesive superhydrophobic surface on which the advancing CAs for water were >160° and droplets readily

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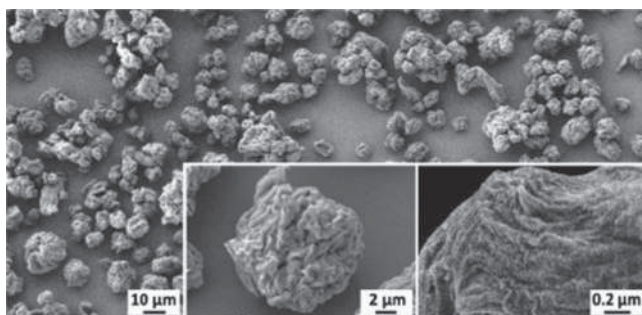
Figure 13. SEM images of spray-dried cellulose microparticles sprayed on glass substrate. Reproduced with permission.[80] Copyright 2012, The Royal Society of Chemistry.

rolled off the surfaces at SAs <5°. CAHs were measured to be 17° and 8° on the CVD-modified and dispersion-modified surfaces, respectively. Robustness of the coating was evaluated by droplet impingement test: over 100 droplets dropped on the same spot could bounce off the surface without leaving a residue. The authors reported, however, that the coating could be damaged by mechanical abrasion.

Barona and Amirfazli[81] fabricated superhydrophobic polymer-nanoclay composite film on paper by spray-coating. The coating recipe contained montmorillonite clay, adhesive, and water dispersed fluoro-methacrylic latex as a hydrophobization agent. Advancing water CA of 159° and CAH of only 2° were measured on the paper sample coated with the 25-μm-thick nanocomposite film. Wetting properties of the coated paper samples were manipulated by printing solid grey patterns of different intensities on the superhydrophobic substrate. The superhydrophobic coating could withstand running through an ink-jet printer without any significant damage: after running the coated paper sample through the printer, the high advancing CA was maintained but the CAH suffered a slight increment to 14°.

Li et al.[82] sprayed octadecyltrichlorosilane (OTS) modified SiO_2 nanoparticles (particle size ≈50 nm) in ethanol suspension on paper to obtain a transparent superhydrophobic coating. The spray-coating was repeated 10–20 times repeatedly, after which the coating was dried at room temperature for 1 h. Water CA and SA for 5 μL droplets on the as-prepared superhydrophobic coating were measured to be 163° and 3°, respectively.
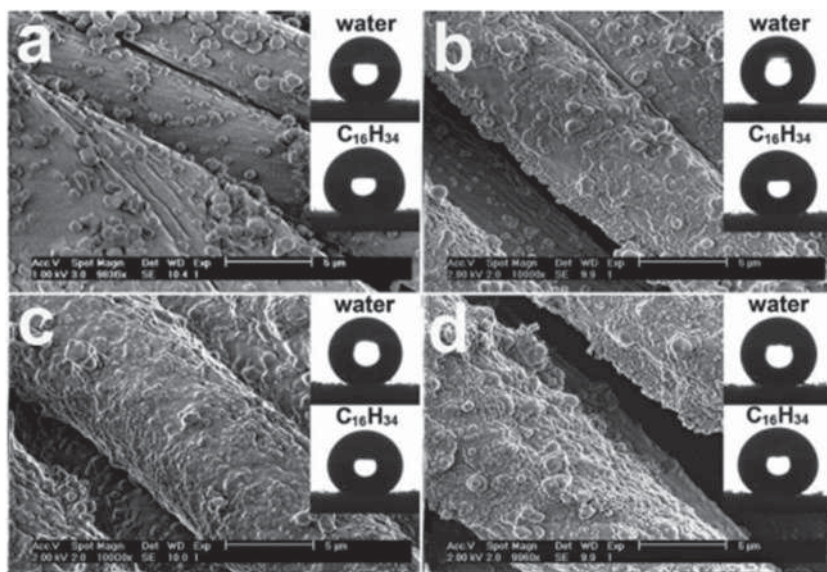
Polymerization Techniques: Nyström et al.[65] modified filter paper surface by atom transfer radical polymerization (ATRP) of glycidyl methacrylate (GMA) using a branched "graft-on-graft" architecture. They used a sophisticated multi-step chemical procedure, where GMA polymer grafts were grown on the cellulose surface. After the grafting, the surface was fluorinated using pentadecafluorooctanoyl chloride. The as-prepared surface showed water CA as high as 172°. In addition, the self-cleaning ability, well known from the lotus leaves, was demonstrated on the surface. In another study, Nyström et al.[86] used different types of hydrophobic modifications on the ATRP "graft-on-graft" treated filter paper. Water CAs on the surfaces modified with PDMS, perfluorinated chains, or alkyl chains varied between 162° and 172°. All the modified surfaces had low CAH values ranging from 5° to 10°. Moreover, the

fluorinated surfaces showed oleophobic properties with sunflower oil CAs of 124° and 144°.

Deng et al.[87] fabricated superhydrophobic cotton with good laundering durability by radiation-induced graft polymerization of fluorinated acrylate monomer, 1H,1H,2H,2H-nonafluorohexyl-1-acrylate. The radiation by γ-rays for 6 h at room temperature caused formation of radicals on the cotton substrate and in the monomer solution to undergo both the "grafting from" and "grafting to" mechanisms. Water CA on the as-prepared covalently bonded fluoropolymer coating was around 160°, and the droplets firmly attached to the surface: 10 μL droplets could not roll off the surface even when tilted upside down. The coating showed good chemical stability over the entire pH-range from 0 to 14. In addition, the surface remained superhydrophobic after overnight immersion in 10% sulfuric acid (H_2SO_4) at room temperature and after treatments with hot solvents such as butane or water. After 50 accelerated laundering cycles, which is equivalent to 250 commercial launderings, hydrophobicity of the modified cotton had slightly decreased, but water CA on the sample was still measured to be greater than 140°. After the laundering, superhydrophobicity of the treated cotton could be easily recovered by extracting the sample in deionized water.

In Situ Nanorod/Particle Growth: Hoefnagels et al.[88] formed covalently bonded silica microparticles on cotton textiles by in-situ growth process, where the cotton textiles were stirred in the reaction mixture for 6 h at room temperature. Subsequently, the textiles were PDMS-modified or fluorinated using perfluoroalkyl silane to obtain superhydrophobic properties. Water CA and SA for 10 μL droplet on the PDMS-modified surface were measured to be 155° and 15°, respectively. Larger droplets showed smaller SAs, and for example, for 500 μL droplet the SA was less than 2°. The particle adhesion to the cotton substrate was tested by sonicating the sample in an ethanol bath. Any significant changes in the surface wettability were not observed after the sonication treatment, which indicated a good adhesion between the silica particles and cotton fibers. The fluorinated surface showed similar water CA to the PDMS-modified surface, however, in contrast to the PDMS-modified surface, the fluorinated surface also showed oleophobic properties. Sunflower oil CA on the fluorinated surface was 140°, and the oil droplets of 15 μL rolled off the surface at SA of 24°. Hexadecane CA on the fluorinated surface was measured to be 135°, but the droplets were firmly attached to the surface and remained stuck even when tilted upside down.

Xu and Cai[89] coated cotton fabrics with zinc oxide (ZnO) nanocrystals using a dip-pad-cure process. The curing was carried out at 170 °C for 3 min. The dip-pad-cure procedure was repeated three times to obtain a dense film of the nanocrystal seeds on cotton, on which ZnO nanorod array was then hydrothermally grown by immersing the sample in the reagent solution at 90 °C for 3 h. After drying at 70 °C for 20 min, the ZnO nanorod coated fabric was modified by self-assembled monolayer of n-dodecyltrimethoxysilane (DTMS) to obtain the hydrophobic chemistry. After washing and drying, the sample was finally cured at 120 °C for 1 h. Water CA on the as-prepared superhydrophobic surface was measured to be 161° and SA for a 40 μL droplet was 9°.

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Figure 14. SEM images of superamphiphobic cotton fabrics. (a) Fabric coated with in situ synthesized silica microparticles, and (b) the microparticle coated fabric after 1 cycle of 220 nm silica nanoparticle deposition, (c) after 2 nanoparticle deposition cycles, and (d) after 3 nanoparticle deposition cycles. Insets display shapes of water and hexadecane droplets on the corresponding surfaces. Reproduced with permission.[49] Copyright 2009, American Chemical Society.

Leng et al.[49] fabricated superamphiphobic cotton textiles based on a multilength-scale roughness from the woven structure of the substrate and two additional layers of micro and nanosized silica particles (**Figure 14**). The silica microparticles were in situ synthesized on cotton from a solution of TEOS for 6 h at room temperature, and the subsequent silica nanoparticle deposition was carried out in isopropanol dispersion by electrostatic attraction. The nanoparticle deposition was executed 1–3 times repeatedly, and after each cycle the sample was treated with silicon tetrachloride-toluene solution to improve mechanical robustness of the surface by forming cross-links among the silica particles and cotton substrate. Finally, the surface was modified using perfluoroalkyl silane to obtain the low surface energy chemistry. CAs for 5 μL water and hexadecane droplets on the modified fabrics were measured to be ≈160° and ≈152°, respectively. In addition, both water and hexadecane droplets easily rolled off the modified fabric surface: SAs for 5 μL, 10 μL, and 20 μL water droplets were around 15°, 10°, and 7°, respectively, while the corresponding values for hexadecane droplets were around 30°, 15°, and 10°, respectively. Mechanical robustness of the modified cotton was evaluated by sonication treatment in ethanol bath, which the sample seemed to tolerate relatively well without any significant changes in its anti-wetting properties.

Kivotidi et al.[90] fabricated flame-retarded superhydrophobic cellulose-based materials, e.g., filter paper and cotton fabrics, by treating the samples with aqueous solutions and supercritical CO_2. In the first step, the samples were immersed in an aqueous solution of calcium chloride ($CaCl_2$) for 40 min, after which the samples were immersed and reacted in an aqueous solution of sodium hydroxide (NaOH) for another 40 min. Followed by the treatments in the aqueous solutions, the samples were exposed to supercritical CO_2 atmosphere at high pressure for 40 min and dried under vacuum. During the multi-step treatment procedure, various salts were produced in-situ on the cellulose substrates to form micro-sized particles. The salts contributed to the flame-retardancy of the treated materials by different mechanisms, but, in addition, they increased surface roughness of the substrate materials, which contributed to enhanced water repellency after hydrophobic modification. The hydrophobic surface chemistry was achieved by dip-coating the samples in a silane-siloxane monomer containing solution for 20 min, after which the samples were left in air atmosphere overnight and dried under vacuum to form a thin silicon-based polymer film on the surface. The as-treated filter paper showed water CAs around 145–154°, and the authors reported easy mobility of the droplets on the surface.

Shateri-Khalilabad and Yazdanshenas[91] fabricated a superhydrophobic and electroconductive graphene-polymethylsiloxane composite coating on cotton. In the first step of the coating procedure, graphene oxide sheets in an aqueous dispersion were deposited on cotton by dip-coating the substrate in the dispersion for 10 min, after which the sample was padded. The dip-coating and padding were repeated three times repeatedly, after which the sample was dried at 70–80 °C for 60 min. In the next step, the graphene oxide was chemically reduced to graphene by immersing the sample into a solution of ascorbic acid at 95 °C for 60 min, after which the sample was rinsed with water and dried in an oven at 70–80 °C for 60 min. The as-prepared graphene coated cotton showed near-superhydrophobic properties with water CA of 143°. In addition, another type of method, so called water shedding angle, was used to characterize wetting properties of the surface. The shedding angle was determined as the smallest inclination of the substrate where water droplets of 10 μL dropped from the needle-to-substrate distance of 2 mm completely rolled off the surface. The shedding angle on the graphene coated cotton fabric was measured to be 41°. Water repellency of the treated fabric could further be improved by growing a layer of polymethylsiloxane nanofilaments (diameter ≈30–90 nm) on the sample surface during 15 min of immersion in a solution of methyltrichlorosilane (MTCS) in hexane, after which the sample was washed and dried/cured in an oven at 110 °C for 60 min. Water CA and shedding angle on the graphene/nanofilament coated cotton fabric were measured to be 163° and 7°, respectively.

Other Methods: Gonçalves et al.[95] reported on fabrication of superhydrophobic coating on filter paper using a multi-step nanoengineering process. In the first stage, the surface roughness of paper was increased by depositing amorphous silica particles (≈800 nm in diameter) on the surface of cellulose fibers in an aqueous suspension. After the particle deposition, the surface roughness and stability were further enhanced by layer by layer (LbL) deposition of poly(diallyldimethylammonium

chloride) (PDDA) and sodium silicate (SS). The LbL deposition was accomplished by immersing the sample 5 times repeatedly in PDDA and SS solutions for 15 min. After each step, the sample was washed and dried in a nitrogen flow. Finally, the surface was modified with fluorosiloxane in ethanol solution, dried, and cured at 120 °C for 2 h. Two different types of fluorosiloxanes were used in the surface modification, 3,3,3-trifluoropropyl trimethoxysilane and 1H,1H,2H,2H-perfluorooctyl triethoxysilane, from which the latter gave better hydrophobic properties for the surface with water CA of 147°. That is, the surface showed near-superhydrophobic properties according to the classical definition of superhydrophobicity. Interestingly, the study revealed that when small silica particles of ≈100 nm or ≈300 nm in diameter were used instead of the large particles of ≈600 nm and ≈800 nm in diameter, any increment in the hydrophobicity of the modified cotton was not observed compared to a sample modified solely with the fluorosiloxane without the presence of any silica particles.

Georgakilas et al.[96] described a procedure to prepare perfluorinated carbon nanotubes (CNTs) to be used in superhydrophobic coatings. The authors demonstrated a fabrication of superhydrophobic CNT coating on cotton by adding droplets of the fluoro-modified CNTs dispersed in hexafluoro-isopropanol on the fabric, after which the sample was dried overnight at 80 °C. Water CA and SA on the CNT coated cotton were reported to be 170° and <5°, respectively.

Yang and Deng[97] applied multilayer deposition of silica particles on paper substrate by dipping the sample repeatedly in aqueous suspensions of polydiallyldimethylammonium chloride and silica particles for 20 min and 10 min, respectively. Chemical modification of the silica coated paper sample was carried out by CVD of perfluorooctyltriethoxysilane (POTS) at 125 °C for 2.5 h, after which the sample was treated another 2.5 h at 150 °C to volatilize the unreacted POTS molecules from the surface. Water CA and SA of 155° and <5°, respectively, were measured on the silica coated paper surface. The CA remained above 150° even after the specimen was kept fully immersed in water for 72 h. Unlike uncoated paper, the superhydrophobic paper could maintain its tensile strength also in humid conditions. In addition, the authors reported reduced contamination of bacteria from an aqueous solution on the superhydrophobic surface.

Hu et al.[98] used commercial PCC particles, hydrophobic stearic acid, and polymer latex particles to fabricate superhydrophobic coating on linerboard paper. Application of the coating slurry was carried out by a simple rod wire coater, after which the sample was dried for 3 min by heating with an IR lamp. The optimized ratios of different compounds in the coating led in decent hydrophobicity with water CAs close to 150°. However, in order to reach CAs greater than 150°, the coated paper was further dipped in potassium stearate, rinsed with water, and dried. In addition to the increased CA, the dipping treatment remarkably decreased water absorption (Cobb value) of the coated paper.

Huang et al.[99] fabricated superhydrophobic paper using TiO$_2$ nanoparticles (10–20 nm in diameter) modified with 3-(trimethoxysilyl) propyl methacrylate (MPS). Cellulose fibers were treated with the modified nanoparticles already in the pulp, and thus any type of further treatments were not needed after

preparation of the paper handsheets. This was apparently the first study, where a superhydrophobic modification was applied to cellulose fibers prior to the papermaking process. Water CA, CAH, and SA of 154°, 4°, and <3°, respectively, were measured on the as-prepared paper. In addition to the enhanced water repellency, the nanoparticle modification improved opacity of the paper, but, on the other hand, decreased its tensile strength.

Stanssens et al.[100] synthesized organic nanoparticles by imidization of poly(styrene-maleic anhydride) copolymers in aqueous dispersion or in presence of palm oil and applied them as hydrophobic coatings on papers by a standard rod-coater. The coatings were dried at 100 °C for 2 min and subsequently stabilized for at least one day. The nanoparticles synthesized in presence of palm oil gave more continuous coating, lower water absorption rate, and greater hydrophobicity compared to the particles synthesized in aqueous solution. The authors reported near-superhydrophobic water CA of 148° on the nanoparticle/oil coated tissue paper.

Fang et al.[101] fabricated superhydrophobic coatings on various substrates, including filter paper and cotton fabric, using a magnet-assembly technique. Hydrophobic iron oxide (Fe$_3$O$_4$) nanoparticles synthesized and functionalized with tridecafluorooctyl triethoxysilane in aqueous solution were deposited on the substrates under a magnetic field. After removal of the solvent by drying in atmospheric conditions, the nanoparticle coating appeared as a hierarchically structured surface composing of aggregated particles of about 10 nm in diameter. Water CAs on the as-prepared coating on filter paper and cotton fabric were measured to be 171° and 165°, respectively. When the nanoparticle coating was deposited without the magnetic field, the particles were distributed more homogenously on the substrate, and thus the superhydrophobic properties were not achieved due to reduced hierarchical roughness of the surface.

Zhao et al.[102] coated cotton fabrics using LbL assembly of azido-functionalized silica nanoparticles (≈70 nm in diameter) and azido-grafted poly(allylamine hydrochloride). The fabrics were sequentially dipped in the aqueous reagent solutions for 5 min and washed with water. UV irradiation was used to improve coating durability by inducing covalent cross-linking within the photoreactive coating layers and the substrate. Hydrophobic chemistry for the coating was obtained by treating the sample with a solution of tridecafluorooctyl triethoxysilane in hexane for 1 h, after which the coating was dried at 100 °C for 30 min. Water CA on the multilayer coated fabric was measured to be 158°, and the coating showed good chemical resistance against various organic solvents and aqueous solutions of wide range of pHs. In addition, the coating could withstand several washing cycles, which was demonstrated by the high water CA of >150° after 50 washing cycles and low CAH of <10° after 25 washing cycles.

Zhang et al.[103] fabricated an OTS-modified silica particles (mean particle diameter ≈243 nm) containing PS solution to form a superhydrophobic coating on filter paper. The coating mixture was applied on the paper substrate by dropping several droplets of the solution on the sample surface, after which the sample was dried at 75 °C for about 20 min. The coating solution which had the mass ratio of the modified silica particles to PS of 2:1 resulted in the best hydrophobic properties of the coating with water CA of 156°. In addition to the good water

repellency, the coating showed good repellency for aqueous solutions of wide pH-range with CAs greater than 140°.

4.2.2. Dry Methods

Plasma Processing: Balu et al.[32] fabricated a superhydrophobic surface on commercial copy-grade paper and hand-made sheets by the means of plasma etching and plasma deposition. In the first step of the procedure, amorphous areas of the cellulose fibers were etched by low-pressure oxygen plasma for 30 min to modify the surface roughness, and in the second step, to obtain a thin low surface energy fluorocarbon layer on the etched substrates, the samples were coated in vacuum by PECVD for 2 min using pentafluoroethane (PFE) as a precursor. After the plasma modification, both paper grades were superhydrophobic with water CAs >160° and CAHs <10°. The PFE-film adhesion to the substrate was evaluated by a standard tape test, which caused cohesive failure in the paper substrate and thus indicated a good adhesion between the PFE-film and cellulose fibers. In addition, robustness of the superhydrophobic surface was evaluated by pressing the paper sample by a bare finger, which caused a slight decrement in the superhydrophobic properties of the surface as the CA on the handsheet paper decreased from 167° to 157° and CAH increased from 3° to 21°. In another study, Balu et al.[13] demonstrated that the hysteresis behavior of the modified paper surface could be drastically altered by affecting the hierarchical structure of the substrate by the plasma etching (**Figure 15**). Droplet adhesion to the modified paper could be altered between the sticky and roll-off states, and CAH on the surface could be tuned between 150° and 3.5° by simply adjusting the plasma etching time.

Cho et al.[94] treated filter paper and cotton fabrics by low-pressure hexamethyldisiloxane (HMDSO)/toluene plasma to render them superhydrophobic. The plasma treatment time was fixed at 30 s. The study revealed that HMDSO/toluene mixing ratio of 3:1 increased surface hydrophobicity more efficiently than other mixture ratios. The plasma-modified paper and cotton surfaces showed superhydrophobic properties with water CAs of 157° and 173°, respectively.

CVD and Nanofilament Growth: Artus and Zimmermann et al.[60,92] applied a transparent and superhydrophobic silicone nanofilament coating on cotton and other types of fabrics (**Figure 16**). A dense layer of polyalkylsilsesquioxane filaments was grown on the surface of individual fibers in one-step process in gas phase under ambient pressure and temperature. To form the coating, the substrates were placed in a sealed chamber for 12 h to react with trichloromethylsilane (TCMS) precursor and water vapor. Water CA and SA for 10 µL droplets on coated cotton were measured to be >150° and <30°, respectively. However, difficulties in determination of the baseline on the uneven substrates and individual sticking fibers hinder reliability of the traditional CA and SA measurements,
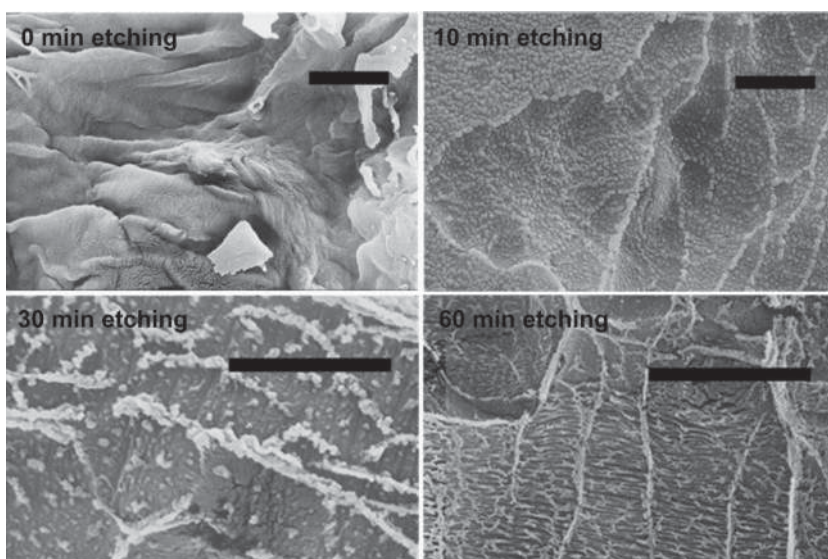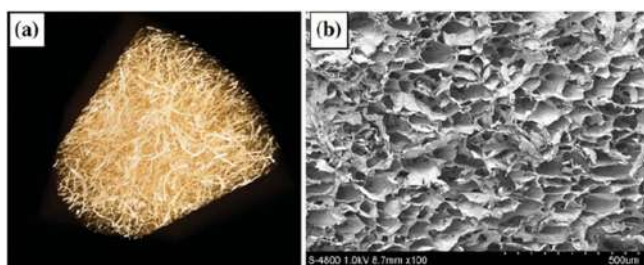

Figure 15. SEM images of paper surface after different periods of oxygen plasma etching and PFE plasma deposition of 2 min. The scale bars correspond to 2 µm. Reproduced with permission.[13] Copyright 2009, Taylor & Francis Ltd.
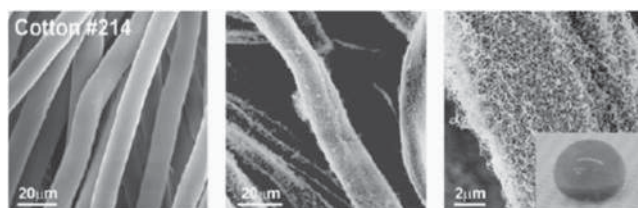
Figure 16. SEM images of cotton fabrics: left: uncoated fabric; middle and right: silicone nanofilament coated fabric. Inset shows water droplet on the coated fabric. Reproduced with permission.[60]

and therefore, wetting properties of the coated samples were studied also by water shedding angle (13 µL droplets were dropped from the height of 1 cm). The shedding angles of the coated cotton samples varied between 25° and 35°, depending on the type of the cotton substrate. As a drawback, the authors reported that the coating treatment dramatically reduced tensile strength of cotton, which limits its use in any real applications. Similar weakening effect, which was observed on coated cotton fabrics, did not occur on coated PET fabrics, on which extensive durability experiments, e.g., abrasion and laundering tests, were performed and material properties were carefully evaluated.

Jin et al.[50] fabricated nanocellulose aerogels consisting of fibrillar networks and structures at different length scales by freeze-drying the hydrogel in vacuum. To obtain superhydrophobic and superoleophobic properties, the aerogel membranes were fluorinated by CVD of FOTS at 70 °C for 2 h. Water CA on the fluorinated membrane was 160° and the surface showed high-adhesive properties as 10 µL water droplet could remain on the surface when tilted upside down. In addition, the surface showed good oleophobicity as the CAs of 153° and 158° were measured for paraffin oil and mineral oil, respectively. Similar to water, the oil droplets were firmly attached to the

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Figure 17. (a) 3D microtomography image and (b) SEM image of nanofibrillated cellulose aerogel. Reproduced with permission.[93] Copyright 2011, Springer.

surface. The authors highlighted the aerogel made of nanocellulose as particularly simple and scalable approach to fabricate overhang structures, which are known to promote superoleophobicity. Plastron layer, i.e., the layer of entrapped air on the surface, could be seen even after 1 week of immersion of the fluorinated aerogel both in water and oil.

Cervin et al.[93] freeze-dried aqueous dispersions of nanocellulose in vacuum to obtain highly porous aerogels (porosity >99%) to be used in oil/water separation (**Figure 17**). To obtain the hydrophobic surface chemistry, the aerogels were treated by vapor deposition of octyltrichlorosilane for 30 min. After the silanization, the surface showed superhydrophobicity with water CA of approximately 150° and superoleophilicity with hexadecane CA of 0°. The authors did not give exact values, but reported that water droplets easily rolled off the aerogels when slightly inclined.

Spray-Coating: Quan et al.[83] used a rapid expansion of supercritical CO_2 solution (RESS) process to fabricate fractal AKD coatings on paper. The flake-like AKD particles with an average size of 1–2 µm were formed as a result of an extremely fast phase transfer when the solution expanded from the supercritical to the gas-like state when sprayed on the substrates in atmospheric conditions. Water CA on paper coated with AKD flakes was 153°. In the case that paper surface was roughened with an emery cloth prior to the AKD coating, the CA was measured to be as high as 172°. Apparently, this was the first study where a superhydrophobic coating was fabricated on paper by straightforward one-step method without any additional steps. In another study,[84] the same group examined hysteresis properties of the AKD coated paper surfaces. The advancing contact angles on the surfaces varied between 150° and 160°, while the receding contact angles were between 110° and 130°. The lowest CAH values were measured to be approximately 30° on the AKD coated surfaces.

Teisala et al., Stepien et al., Mäkelä et al., and Aromaa et al.[33,43,66,85] have published several studies on fabrication of transparent superhydrophobic TiO_2 nanoparticle coatings (**Figure 18**) on cellulose-based substrates such as pigment coated board, paper, and polyethylene-paper laminate using

thermal nanoparticle synthesis/deposition method called liquid flame spray (LFS). In the LFS process a liquid precursor, titanium tetraisopropoxide (TTIP), reacts in a hot and turbulent hydrogen-oxygen flame to form solid nanoparticles with an average diameter ranging from <20 nm to ≈80 nm depending on the coating parameters. Instead of impaction, which is typical for conventional spray-coating techniques where droplet or particle size is in the range of micrometers, in the LFS-coating the nanoparticle deposition on the substrate occurs by thermophoresis and diffusion. The nanoparticle coating was fabricated in one-step roll-to-roll procedure in ambient conditions, and the coating showed superhydrophobic properties with water CAs greater than 160° instantly after the coating procedure, thus any further modification steps were not needed. The low surface energy chemistry of the coating originates from spontaneously accumulated carbonaceous material on TiO_2, e.g., hydrocarbons, during the high-temperature coating process. The multi-scale hierarchical roughness of the coating originates from the individual particles, particle aggregates, and roughness of the substrate material. The authors highlighted LFS as a particularly efficient method to fabricate superhydrophobic coatings on paper and board, and demonstrated fabrication of the superhydrophobic coating on board with the line speed of 150 m/min. The hysteresis and adhesion properties of the superhydrophobic TiO_2 coating could be varied by altering its hierarchical structure: CAH values ranging from 6° to >100° were measured, while SA for a 10 µL water droplet varied from 10° to a high-adhesive state where the droplet remained on the surface even when flipped upside down. Photocatalytic activity of the TiO_2 coating enabled surface energy patterning and reversible wettability switching on the surface. In addition, the coating could repel liquids of lower surface tension than pure water although its chemistry was free from fluorocompounds, e.g., CA of 155° was measured for 15 wt% water-ethanol solution. As a drawback, the coating could be damaged relatively easily by physical stress. Several cycles of tape and abrasion tests revealed that although the superhydrophobic effect of the
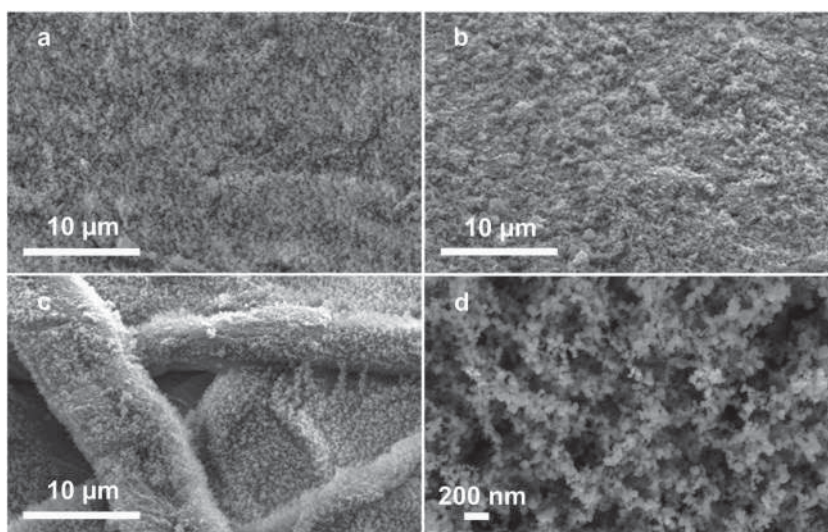
Figure 18. SEM micrographs of different types of hierarchically structured superhydrophobic TiO_2 coatings on (a,b) pigment coated board and (c) paper substrates. (d) Magnification of (a). Reproduced with permission.[33] Copyright 2012, American Chemical Society.

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coating was damaged, some hydrophobic effect of the coating still remained on the damaged surface as the water CAs were measured to be between ≈110° and 130°.

Other Methods: Daoud et al.[104] utilized pulsed laser deposition to fabricate thin PTFE films on cotton fabrics. The film deposition was carried out in vacuum at room temperature, and the deposition time was about 3 min. The PTFE coated fabrics showed superhydrophobic properties with water CA of 151°. SEM imaging revealed that the PTFE film on cotton had a granular surface structure where the grain size was about 50–70 nm in diameter. This was apparently the first straightforward one-step approach to fabricate a superhydrophobic coating on cotton. That is, any type of chemical modification, drying, or curing steps were not needed after application of the coating.

Zhang et al.[105] presented a solvothermal synthesis of nanoporous polydivinylbenzene (PDVB) powder and demonstrated an innovative approach to apply the superhydrophobic nanopowder coating on various substrates. The as-prepared PDVB powder took a form of a solid monolith, by which the substrates were simply wiped to paint the superhydrophobic and transparent nanoporous polymer coating. Attachment of the polymer powder on the rough paper surface occurred by the electrostatic interaction, and average thickness of the coating was estimated to be ≈10 μm. Water CA on the polymer coated paper was 157° and droplets could roll off the surface at SA of 6°. The superhydrophobic properties of the coating remained stable during the long-term follow-up period of a single water droplet as the CA decreased only 3° in 24 h. In addition, the superhydrophobic properties of the coating were reported to remain stable also in humid conditions.

4.3. Potential Applications

A superhydrophobic coating on paper or cotton textiles brings new properties and functionalities for the materials and widens their utilization potential in new application areas. Superhydrophobic paper can find use, for example, in water-repellent packaging materials, e.g., food and beverages, in self-cleaning labels, cartons, and boards, or as membranes with low degree of surface fouling.[13,32,86] Applications for superhydrophobic cotton include liquid- and dirt-repellent, breathable, self-cleaning, and anti-biofouling clothes and textiles. In addition, superhydrophobic paper and cotton have good utilization potential in some other important applications such as cheap and disposable microfluidic devices for, for example, point-of-care diagnostics.[32,62,106]

Surface energy/wettability patterning on superhydrophobic cotton or paper by, for example, high energy ink patterns[81,107,108] or UV-illumination[43] offers several possibilities in transportation and manipulation of droplets and liquid flows, or in deposition of functional materials such as inks on the intelligent substrate which guide the fluid setting on the hydrophilic areas of the surface. Balu et al.[107] fabricated two-dimensional paper-based lab-on-a-chip (LOC) microfluidic devices by printing high surface energy black ink patterns on superhydrophobic paper substrate. The ink patterns provide local control over droplet adhesion on the superhydrophobic paper, and thus enable storage, transport, mixing, sampling, and splitting of droplets of test liquids on the
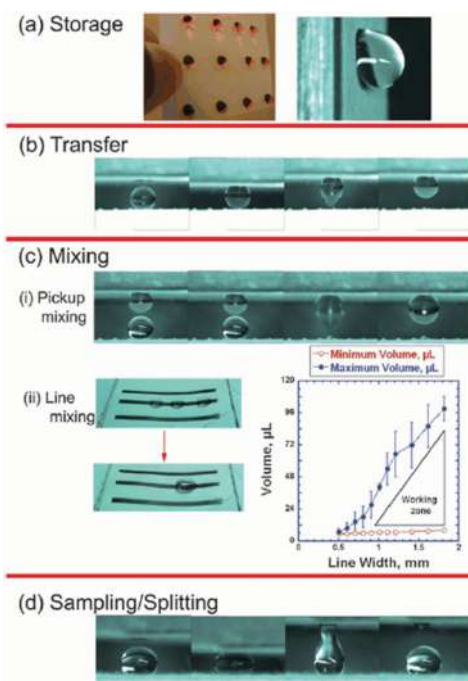
Figure 19. Demonstration of water droplet (a) storage, (b) transfer, (c) mixing, and (d) sampling/splitting on an ink-patterned superhydrophobic paper surface. Reproduced with permission.[107] Copyright 2009, The Royal Society of Chemistry.

surface (**Figure 19**). Barona and Amirfazli[81] demonstrated a simple way to control water droplet mobility and hysteresis on paper-based LOC devices by printing solid grey patterns of different intensities on superhydrophobic paper surface. Li et al.[108] demonstrated how test liquids could be sampled in a controlled manner by printing high hysteresis wax islands onto low hysteresis superhydrophobic paper. The volume of the sampled droplets could be controlled by the choice of the wax type, and by the surface roughness and size of the wax islands. The authors highlighted point-of-care biomedical testing as a potential application for the paper-based LOC devices, and demonstrated a colorimetric glucose test performed with the high hysteresis islands on superhydrophobic paper (**Figure 20**).
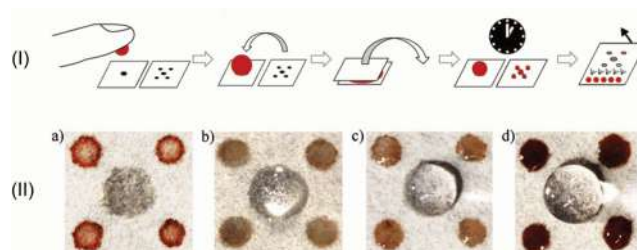
Figure 20. (I) Illustration of biomedical testing based on droplet sampling on a superhydrophobic paper surface, and (II) a colorimetric glucose test performed on a wax-patterned superhydrophobic paper substrate: (a) dried reagents before exposure to test liquids, and after sampling from bulk droplets of (b) pure water, (c) 0.0015 M glucose solution, and (d) 0.0050 M glucose solution. Reproduced with permission.[108] Copyright 2012, Springer.

Figure 21. Separation of liquids that differ in surface tension. (a) Illustration of filtration of oil from water through superhydrophobic filter paper (Reproduced with permission.[75] Copyright 2010, American Chemical Society) and (b) absorption of colored hexadecane from water surface by highly porous superhydrophobic nanocellulose aerogel (Reproduced with permission.[93] Copyright 2011, Springer).

Another widely demonstrated application for superhydrophobic paper is oil separation from water. For instance, Huang et al.[77] suggested that superhydrophobic paper could be used in automobile oil filters. Wang et al.[75] fabricated superhydrophobic filter paper capable of selectively absorbing and separating liquids that differ in surface tension (**Figure 21**a). The modified filter paper could absorb diesel oil and organic solvents floating on water up to 3.4 times of its own weight. By removing the absorbed oil or organic solvent from the filter paper by drying it in an oven at 80 °C, the filter paper could be reused several times and the absorption capacity and water CA on the surface remained nearly unchanged. The modified filter paper could efficiently separate oil/water mixtures of different volume ratios by letting oil permeate through the paper while water remained on the surface. Interestingly, the modified filter paper could also be used to extract ethanol from homogeneous aqueous solutions. Cervin et al.[93] utilized superhydrophobic ultra-porous nanocellulose aerogels as separation medium for oil/water mixtures. The aerogels had porosity greater than 99%, and their absorption capacity of hexadecane was up to 45 times of the aerogel weight (Figure 21b). The aerogels could be reused several times as they did not show significant change in volume upon sorption/desorption cycles.

Jin et al.[50] fabricated superhydrophobic and superoleophobic nanocellulose aerogel membranes to be used as bioinspired cargo carriers on water and oil (**Figure 22**). On water, the
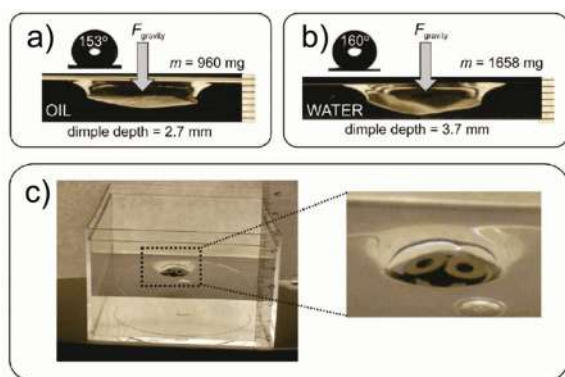
Figure 22. Superamphiphobic nanofibrous cellulose aerogel membrane as a load carrier. The side-view photographs show the dimple depth of the aerogel membrane at the maximum supportable weight on (a) paraffin oil and (b) water. (c) Metal weights loaded on the aerogel membrane floating on water. Reproduced with permission.[50] Copyright 2011, American Chemical Society.

aerogel was capable of supporting a load over 500 times its own weight. On oil, the aerogel could support a load over 300 times its own weight. The authors envisaged the aerogel membranes as foul-resistant and gas permeable carriers and coatings for miniaturized robots or environmental gas sensors floating on practical liquids.

5. Summary and Outlook

To date, many innovative methods to fabricate superhydrophobic coatings on affordable and versatile cellulose-based materials have been introduced ranging from simple one-step processes to sophisticated multistep procedures, which all produce unique coatings with distinct properties. Superhydrophobic coatings on cellulose-based materials offer a sustainable and ecological alternative to reduce the use of fossil fuel -based polymers. In addition, superhydrophobic coatings typically possess several functionalities which cannot be achieved by traditional water repellency treatments. In fabrication of superhydrophobic coatings on cellulose-based materials, advantage of many wet-chemical methods is the excellent durability of the coatings, which is crucial in applications such as waterproof clothing where the material needs to stand abrasion and multiple laundering cycles. Instead, advantage of many dry methods is their simplicity: straightforward one-step processes, where organic solvents and any type of additional drying or curing steps are not needed, can be readily scaled up for high-volume production of superhydrophobic coatings. While durability of the coating is one of the key issues in fabrication of superhydrophobic fabrics, in case of paper products the ability to fabricate the superhydrophobic coating effectively in high volumes can be even more important than the coating durability.

As a result of the intensive study, many methods to fabricate superhydrophobic coatings on cellulose-based materials have been developed, and the coating properties and related phenomena are rather well understood. Future work should increasingly focus on identifying the most suitable practical applications for the superhydrophobic cellulose-based materials. Potential applications include waterproof, stain-resistant, breathable, anti-biofouling, and self-cleaning clothing; filters for oil/water separation; and cheap and disposable products designed for short-term use, for example, water-repellent and gas permeable packaging materials. In particular, one emerging and globally important field of applications for cellulose-based materials is low-cost point-of-care diagnostic devices, where utilization potential of superhydrophobic coatings is yet largely unexplored. Future aim is to utilize superhydrophobic coatings in development of high-quality functional products made from renewable sources, and thus to reduce the use of fossil fuel -based polymers. Due to the many inherent profitable material properties such as affordability, recyclability, flexibility, breathability, and mechanical strength, superhydrophobic cellulose-based materials have a great potential to be utilized in variety of applications in different fields. Therefore, it is worth emphasizing the importance of open-minded interdisciplinary research in the field of science to seek new and innovative

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practical applications for superhydrophobic cellulose-based materials.

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