Approaching super-hydrophobicity from cellulosic materials: A Review

Junlong Song and Orlando J. Rojas

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SUMMARY: The development of super-hydrophobic surfaces has been inspired by natural systems and uses a number of novel (nano) technologies. Superhydrophobicity has stimulated much scientific and industrial interest because of applications in water repellency, self-cleaning, friction reduction, antifouling, etc. Despite its inherent hydrophilicity, cellulose has unparalleled advantages as a substrate for the production of super-hydrophobic materials. This is because of its abundance, biodegradability and unique physical, chemical, and mechanical properties that compare advantageously with the non-renewable materials typically used. This review includes a comprehensive survey of the progress achieved so far in the production of super-hydrophobic materials based on cellulose. Emphasis is placed on the effects of cellulose surface chemistry and topography, both of which affect hydrophobicity. Overall, this contribution summarizes some of the aspects that are critical to advance this evolving field of science.

ADDRESSES OF THE AUTHORS:
Junlong Song: Jiangsu Provincial Key Lab of Pulp and Paper Science and Technology, Nanjing Forestry University, Nanjing, Jiangsu, P.R. China 210037;
Orlando J. Rojas: Departments of Forest Biomaterials and Chemical and Biomolecular Engineering, North Carolina State University, Box 8005, Raleigh, NC 27695-8005 USA; Department of Forest Products Technology, Faculty of Chemistry and Materials Sciences, Aalto University, P.O. Box 16300, Aalto FIN-00076 Finland.

Wettability is a fundamental property of solid surfaces that plays important roles in household, industrial and advanced applications. Super-hydrophobic surfaces, i.e., surfaces with a water contact angle (WCA) larger than 150° and a sliding angle (SA) less than 10°, have drawn great scientific and industrial interest due to their relevance in water repellency, self-cleaning, friction reduction and antifouling (Genzer, Efimenko 2006; Ma, Hill 2006; Ma et al. 2005). The interest in self-cleaning, a unique property of super-hydrophobic surfaces, has been driven by the need to fabricate surfaces such as satellite dishes, solar energy panel, photovoltaics, exterior architectural glass, automobile windshields, swimming coatings, and surfaces with special heat and mass transfer properties (Cheng et al. 2006; Ma, Hill 2006; Nakajima et al. 2001). The reduction of friction is of major importance in many material applications (Choi et al. 2006; Schneider et al. 2008). Contribution to corrosion prevention is also recognized as an attribute of super-hydrophobic surfaces, which are effective to prevent film infiltration and to limit surface exposure to corrosive media (Barkhudarov et al. 2008; Wang et al. 2011b; Yuan et al. 2011; Zhang et al. 2011). Super-hydrophobic surfaces have been applied to prevent bacterial adhesion (Crick et al. 2011); to manufacture intelligent microfluidic devices (Chunder et al. 2009); to improve blood compatibility and anticoagulation (Hou et al. 2010; Leibner et al. 2009), and to reduce ice growth in humid atmospheres (Farhadi et al. 2011; Yang et al. 2011; Yin et al. 2010).

Generally, both the surface chemistry and the surface roughness affect hydrophobicity (Genzer, Efimenko 2006; Nakajima et al. 2001) and the interplay between these properties have been the subject of active research during the last decades. Techniques to endow the surface with nano-scale roughness, such as etching and lithography, sol-gel processing and electrospinning have been implemented while the surface chemistry has been modified by using strategies involving physical and chemical adsorption. Important progress achieved in this field has been reported in several excellent review papers (Dorrr, Rühe 2008; Genzer, Efimenko 2006; Ma, Hill 2006; Nakajima et al. 2001).

A distinctive feature is the fact that substrates based on non-renewable materials, including minerals and synthetic polymers, are being substituted as platforms to develop super-hydrophobic surfaces. This is motivated in part by the recent impetus of sustainability and environmental conscience. Therefore, efforts to induce hydrophobicity in bio-based materials, including lignocellulose, are growing steadily and are being reported more often. Here lignocellulose is referred to as materials derived from plant fibers that contain cellulose, lignin, and heteropolysaccharides. This includes wood, non-wood plants, agricultural residues, grasses, etc. (Rowell 2002). Compared with nonrenewable materials, lignocellulose has distinctive advantages because they are readily available, light-weighted, abundant and renewable.

The know-how available to attain low and ultra-low energy surfaces from mineral and polymeric materials has undergone several major advances. However, the case of lignocelluloses has proved to be more challenging; this is in part because of the influence of hydrophilic components that are present in complex and highly hierarchical structures. Applications such as printing, packaging, food storage and others that demand certain barrier properties are at the center of interest.

The partial water resistance required in writing, printing, and packaging materials, has been achieved by surface and bulk modifications. For example, animal glue and so-called “surface” and “internal” sizing use wood rosins, alkenylsuccinic anhydride (ASA) and alkylketene dimers (AKD) (Hubbe 2006), which are common additives in papermaking. Nevertheless, surface and internal sizing fell short to meet the new demands of super-hydrophobic materials. Furthermore, while processes to modify paper surfaces are widely known,
production of super-hydrophobic materials based on cellulose fibers are less developed.

Many developments to obtain super-hydrophobic surfaces based on cellulose have been reported in recent years, for example in cotton fabrics and paperboard. In order to discuss these cases and also the broader aspects of super-hydrophobic cellulose, this review begins with a brief discussion of the fundamentals of super-hydrophobicity and then follows with a report of the latest advances related to chemical grafting, sol-gel process, nanoparticles modification and pulsed laser and plasma deposition, among others. Even though, super-hydrophobic surface requires water contact angles greater than 150° combined with a low roll-off angle based on the definition, some developments to enhance the wettability close to that criterion are also addressed.

Wettability and super-hydrophobicity

Definitions

Super-hydrophobic surfaces are abundant in nature, as exemplified by the wings of butterflies (Chen et al. 2004; Genzer, Efimenko 2006), the feet of water striders (Gao, Jiang 2004), and the leaves of plants (Cheng et al. 2006; Koch et al. 2009). Despite the ubiquitous presence of super-hydrophobicity, attempts to understand associated phenomena have been applied only recently. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) are some of the tools that have enabled the observation of nano-scale features on the surfaces and to unveil some of the secrets behind super-hydrophobic development.

Bottom line is the fact that the combination of low surface energy and nano-roughness are effective in attainment of super-hydrophobicity. Based on related principles, many methods and techniques are now being developed following bio-mimicry.

Wettability and repellency are important properties of solid surfaces from both fundamental and practical aspects. The wettability of a solid surface is a characteristic property of materials and depends strongly on both the surface energy and roughness (Cassie, Baxter 1944; Genzer, Efimenko 2006; Koch, Barthlott 2009; Nakajima et al. 2001; Sun et al. 2005; Wenzel 1936). Some fundamental concepts relevant to wettability and super-hydrophobicity are addressed briefly in the following paragraphs.

A key definition is that of the contact angle, i.e., the angle at which the liquid/vapor interface meets a given solid. (cf. Fig 1) When the probing fluid is water, the measured contact angle is the “water contact angle” (WCA). The WCA is specific to any given system and is determined by the interactions across the three-phase line. Hydrophilic, water-loving materials are substances with WCA lower than 90° while hydrophobic ones are water-hating, displaying a WCA higher than 90°. As stated earlier, super-hydrophobic characteristics are attained when the water contact angle is greater than 150°.

The Young equation is the most important yet the simplest relationship to describe the balance of forces acting on a liquid droplet spreading on a surface.

\[ \cos(\theta) = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \]

where \( \gamma_{SV} \) is the solid-vapor interfacial energy, \( \gamma_{SL} \) is the solid-liquid interfacial energy, and \( \gamma_{LV} \) is the liquid-vapor interfacial energy.

The contact angle (\( \theta \)) of a drop is related to the interfacial energies acting between the solid-liquid (\( \gamma_{SL} \)), solid-vapor (\( \gamma_{SV} \)) and liquid-vapor (\( \gamma_{LV} \)) interfaces and is described by Eq. 1:

\[ \cos(\theta) = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \]

There is a limitation in the application of the Young equation in that it is strictly valid only for surfaces that are atomically smooth, chemically homogeneous, and do not change by possible interactions with the probing liquid.

According to Young Equation, the highest contact angle will be achieved under the condition of lowest \( \gamma_{SV} \), i.e., the material with the lowest possible surface energy. As a reference, the surface energy of some moieties of interest decreases in the following order: -CH_2->-CH_3->-CF_2-CF_3-H>-CF_3 (Genzer, Efimenko 2006). The lowest surface energy value yet recorded, 6.7 mJ/m², is obtained for a surface with regularly aligned closest-hexagonal packed -CF_3 groups, which leads to a calculated WCA of about 120° (assuming water and standard conditions in Eq 1) (Nishino et al. 1999). Strikingly, natural super-hydrophobic surfaces as those mentioned previously show larger values. How is then such a super-hydrophobic behavior possible?

The explanation lies on the contribution of the roughness of surfaces. It is very difficult to find in nature a surface perfectly flat as assumed in Young’s approach. So in most cases roughness ought to be considered (cf. Fig 1b). Wenzel (1936) proposed a model to describe the contact angle \( \theta' \) of a rough surface by modifying Young’s equation as follows:

\[ \cos(\theta') = \frac{r(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} = r \cos(\theta) \]

In Eq 2, the parameter \( r \), is a roughness factor, defined as the ratio of the actual area of the rough surface to the geometric projected area. Since \( r \) is always larger than unity, the surface roughness enhances hydrophilicity in
the case of hydrophilic surfaces. Similarly, it enhances the hydrophobicity of hydrophobic ones. In other words, in the Wenzel regime roughness amplifies both hydrophilicity and hydrophobicity.

When the surface contains small protrusions, which cannot be filled by the (probing) liquid and are instead filled with air (cf. Fig 1c), the wettability enters the so-called Cassie-Baxter regime (1944). Cassie proposed an equation describing the contact angle \( \theta' \) at a surface composed of solid and air and used the wetted area fraction \( f \), that is, the one in contact with the liquid. More specifically, \( f \) was defined by \( \Sigma a / \Sigma(a+b) \), where \( a \) and \( b \) represent the contact area with the liquid \( a \) and the air \( b \), respectively. Thus, the water contact angle \( \theta \) was expressed according to Eq 3, which assumes a water contact angle with air of 180°.

\[
\cos(\theta') = f \cos \theta + (1-f) \cos 180° = f \cos \theta + f - 1
\]  

[3]

In Eq 3, the fraction \((1-f)\) describes the area in contact with air. Note that Eq 3 only applies to cases where the liquid touches just the top of the surface. If partial penetration through surface grooves occurs, a more complex equation is required, which has been described by Werner et al. (2005). Because pores are filled with air, which is extremely hydrophobic, the contact angle always increases, relative to the behavior observed on a flat substrate having an identical chemical composition. Hence surface topography has a very profound effect on material wettability. In this case, roughness works as an amplifier only for hydrophobicity.

It has been shown that there is a critical value of \( f \) below which the Cassie regime exists and above which the Wenzel regime is thermodynamically more stable (Bico et al. 1999; 2001; Callies, Quéré 2005; Lafuma, Quéré 2003; Quéré et al. 2003). The corresponding transition occurs at a certain critical wettting angle \( (\theta_c) \) defined by:

\[
\cos(\theta_c) = \frac{f}{r-1} - \frac{f}{r}
\]  

[4]

where \( f \) and \( r \) were defined in reference to Eq 2 and Eq 3. Hence at contact angles larger than \( \theta_c \), air pockets are present beneath the drop, which, in turn, exists in the Cassie regime. Quéré and coworkers (Quéré 2004; Quéré, Bico 2003) also pointed out that the Wenzel regime was the equilibrium state of the Cassie regime.

A molecular dynamics study (Yang et al. 2006) of liquid droplets in contact with self-affine fractal surfaces also provided some evidence that the contact angle for nanodroplets depends strongly on the root-mean-square surface roughness amplitude but is nearly independent of the fractal dimension \( D_f \) of the surface.

The second requirement for super-hydrophobicity (water must not stick to the surface) is closely related to the contact angle hysteresis \( \Delta \theta \) of the surface — the difference between the largest (advancing) and smallest (receding) stable contact angle \( \theta_{adv} - \theta_{rec} \). The contact angle hysteresis is extremely important in the self-cleaning applications. The maximum lateral force \( F_{lat} \) that a distorted droplet can buildup depends on \( \theta_{adv} \), and \( \theta_{rec} \), as Eq 5 (Furmidge 1962):

\[
F_{lat} \propto \cos \theta_{rec} - \cos \theta_{adv}
\]  

[5]

which can be approximated for small hysteresis as \( F_{lat} \propto \Delta \theta \sin \theta \).

It has to be noted that super-hydrophobic surfaces can be wetted by organic liquids easily. Super-oleophobic surfaces denote those surfaces with a contact angle greater than 150 degrees with organic liquids that have appreciably lower surface tensions than that of water (Tuteja et al. 2007). Compared with super-hydrophobic surfaces, super-oleophobic surfaces are much less discussed in the literature; recently, however, they have received increased attention since they have a great impact on a wide range of phenomena, including biofouling, loss of self-cleaning ability, and swelling of elastomeric materials. Calculations suggest that creating such a surface would require a surface energy lower than that of any known material. In this regard, Tuteja et al. (2007) proposed a third factor, the re-entrant surface curvature, which combined with chemical composition and roughness, can be used to design surfaces that display extreme resistance to wetting from a number of liquids with low surface tension, including alkanes, such as decane and octane. Super-oleophobic surfaces have been achieved by using fluoro-decylpolyhedral oligomeric silsesquioxanes (POSS) coatings, which display contact angles greater than 160° for various non-polar fluids (Meuler et al. 2011).

Generic methods toward super-hydrophobicity

According to the previous discussion on super-hydrophobicity, there is only one way to access this property: to exploit the combined effects of surface chemistry and morphology of a give surface. Materials with low surface energy include fluorocarbons, silicones, and some organic and inorganic materials. Among low surface energy materials, fluorocarbons are the most frequently used. They have also attracted industrial interest. Silicones (Artus et al. 2006; Dou et al. 2006; Guo et al. 2006; Jin et al. 2005; Khorasani, Mirzadeh 2004; Khorasani et al. 2005; Lee et al. 2005; Liu et al. 2006; Ming et al. 2005) and organic materials (Jiang et al. 2004; 2005; Lee et al. 2004; Lu et al. 2004; Zhao et al. 2005) are other two widely used low surface energy materials. Although fluorocarbons show the lowest surface energy known, it is interesting to note that they are rarely present in the organic materials produced by nature.

The fluorine/carbon atomic ratio is a key aspect to define hydrophobicity, as has been demonstrated by Hsieh et al. from studies with carbon nanofiber arrays (Hsieh et al. 2006). As expected, as more F atoms are introduced, lower surface energy and higher contact angle are achieved. The packing density of related moieties is another factor influencing the surface energy and its stability. Genzer and Efimenko (2000) demonstrated elegantly this concept after creating long-lived super-hydrophobic polymer surfaces through mechanically assembly monolayer. \( \text{FC}_\text{F}_3(\text{CH}_\text{H}_2)_\text{SiCl}_3 \) molecules were deposited from the vapor phase on a stretched elastomeric poly(dimethyl siloxane) (PDMS) substrate; after deposition the strain was released making the film to return to its original size, causing the grafted
Fig 2. Strategies used to attain super-hydrophobicity by combining low surface energy coatings and surface roughness.

F(CF<sub>2</sub>)<sub>3</sub>(CH<sub>3</sub>)SiCl<sub>3</sub> molecules to form a densely organized mechanically assembled monolayer. The water contact angle, compared to the unstretched surface, was found to increase by up to 30 degrees.

We now turn our attention to methods to produce nano-roughness. The statistical roughness parameters are uniquely related to each other over the different measuring techniques and sampling sizes, as they are purely statistically determined. However, they cannot be directly extrapolated over different sampling areas as they represent transitions at the nano-, micro-to-nano and micro-scale levels. Therefore, the spatial roughness parameters including the correlation length and the specific frequency bandwidth should be taken into account, which allow for direct correlation of roughness data at different sampling sizes (Samyn et al. 2011b).

Nano roughness can be created through etching and lithography, sol-gel processing, layer-by-layer and colloidal assembly, electrochemical reaction and deposition, electrospinning and phase separation. These approaches were addressed in detail in a review article by Ma and Hill (2006). In addition, it can be noted that rapid expansion of supercritical solution as reported by Werner et al. (Quan et al. 2009; Werner et al. 2010), utilizes the high solvating power of supercritical carbon dioxide to produce micro or nano-particles that can render the surface with nano-roughness. It is worth noting, however, that these approaches have been usually applied to hard surfaces and the question is then if they can be adapted to cellulosic materials. In sum, Fig 2 indicates the methods available to attain super-hydrophobic surfaces by using two combined strategies, one related to changes in surface energy and the other one related to changes in surface roughness.

Recent progress to approach super-hydrophobic cellulosic materials

In the previous section, the general principles of super-hydrophobic surfaces and the approaches toward super-hydrophobicity were introduced. However, what about the progress toward surperhydrophobic cellulosic materials? Based on the principles of superhydrophobicity it is now clear that the effects of low surface energy and nano-roughness topography are required. In general, surface energy reduction and roughness creation can be accomplished simultaneously or in sequence.

Compared with efforts to create nano-roughness, surface energy reduction is much simpler and straightforward. Chemicals with low surface energy, such as fluorine- and silicone-containing polymers as well as hydrocarbons can be applied to cellulose by grafting, adsorption, chemical vapor deposition, etc. On the other hand, the creation of nano-roughness may be the more demanding step toward super-hydrophobic cellulose. Thus, surface energy reduction is usually addressed somewhere during the application of techniques to endow the materials with roughness.

The approaches used in recent years toward superhydrophobicity of cellulosic materials can be classified into two categories, based on the generation of roughness:

1. Roughness offered by coating cellulosic substrates, which include:
   a) Chemical grafting to modify the surface chemistry and surface morphology of cellulosic fiber/surface simultaneously.
   b) Sol-gel processes to render cellulose fiber/surface with porous outer-layer and to reduce surface energy by post-treatment or by mixing precursors with low surface energy side chains.
   c) Nanoparticle deposition, for example by using metal, metal oxide, mineral and polymers that modify the morphology of the cellulosic fiber/surface, followed by surface energy reduction by post-treatment.
   d) Chemical vapor deposition.

2. Roughness offered by regeneration or fragmentation of cellulosic materials, which among others include:
   e) Electrospinning and electrospaying
   f) Use of nanocellulose (cellulose nanocrystals and nanofibrillated cellulose)
   g) Use of cellulose composites.

Modification of roughness by coating

Chemical grafting. Cellulose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>)<sub>α</sub> is a long-chain polymeric polysaccharide of glucopyranoses repeating units linked together by β-1,4 glycosidic bond (cf. Fig 3). It forms the primary structural component of green plants. The primary cell wall of green plants is made of cellulose while the secondary wall contains cellulose with variable amounts of lignin.

The hydroxyl groups of cellulose can be partially or fully reacted with various species to provide cellulose derivatives with useful properties. This provides an opportunity to modify the surface of cellulose/lignocellulosics by chemical reactions. Through derivatization reactions, polymers with special structures and functions can be introduced to modify the surface and attain the desired properties. This has been the subject of intense studies and a review paper which addresses the subject in detail is available (Cunha, Gandini 2010).

Due to the abundance of OH groups in cellulose, chemicals with low surface energy, such as fluorine-containing substituents (Cunha et al. 2006; Cunha et al. 2007; Ostenson et al. 2006; Yuan et al. 2005), silicone and hydrocarbon polymers (Garoff, Zauscher 2002; Pasquini et al. 2006) can be easily introduced by esterification with acid or anhydride (cf. Fig 4).
Nyström et al. reported on a method to improve the surface density of fluorine-containing moieties by using branched “graft-on-graft” architectures (cf. Fig 5) followed by post-functionalization leading to fluorinated brushes (Nyström et al. 2006). In their work, the first route (route I in Fig 5) involved reaction of the hydroxyl groups on the cellulose substrate with pentadecafluoro-octanoyl chloride. The coverage of fluorinate groups was observed to be limited and so the exact water contact angle was difficult to measure as it changed with contact time. In fact, the surface first showed super-hydrophobicity with WCA 150°; but after 20 min the contact angle decreases to 128° and below 90° after 50 min. This indicates that the cellulose surface was not fully covered by the fluorinated material. In order to improve the surface-coverage and thereby the hydrophobicity, a functional monomer was grafted from the cellulose substrate to enable attachment of an increased amount of fluorine groups. In route II (Fig 5), two fluorine groups were grafted to the surface and the contact angle increased to 154° and somewhat more irreversibly. To further improve the super-hydrophobicity, a branched-like structure was used to attach four fluorine groups per hydroxyl group on cellulose (route III in Fig 5). This step improved the WCA to extremely high values, up to 170°. Nyström et al. (2009) used a similar approach to produce super-hydrophobic and self-cleaning cellulose surfaces via surface-confined grafting of glycidyl methacrylate by using atom transfer radical polymerization combined with post-modification reactions.

Fabbri and coworkers (2004) proposed a new pathway to introduce fluorine-containing polymers onto cellulose. Their work involved organometallic compounds (one or two metals bound to carbon) reacting with OH groups of cellulose (cf. Fig 6). Unreacted metal-to-carbon bonds were exploited to graft numerous molecular structures derived from hydroxyls and amines.

A polymer containing an azide group was employed by Li et al. (2010a) to covalently attach amphiphilic triblock copolymers to cotton via UV irradiation. Amphiphilic triblock azide copolymers containing poly(ethylene glycol) (PEG) and poly(2,2,3,4,4,4-hexafluorobutyl acrylate) blocks were synthesized through room temperature reversible addition fragmentation chain transfer polymerization using redox initiation (cf. Fig 7). These polymers were successfully applied to fabricate super-hydrophobic cotton fabrics by using a facile UV irradiation approach.

The introduction of fluorinated polymer chains endowed cotton with a WCA of 155°. Since the fluorinated polymer chains were covalently attached on the surface, the super-hydrophobic cotton fabric possessed high stability and chemical durability.

It is reasonable to expect for the hydrophilic PEG blocks to locate in the interface between the block copolymer coating and the cotton fibers, which was suggested to occur via H-bonds between PEG and the hydroxyl groups of cellulose; also, it is expected that the fluorinated blocks aggregate in the outermost side of the coating, which contribute to the super-hydrophobicity of the modified substrate.
The surface morphologies of the original and the modified cotton fabrics were investigated by SEM and AFM. Fig 8a and 8b shows highly textured, microscale fibers on the cotton fabric while the modified substrate reveals a coating layer consisting of the copolymers with some embossments caused by the aggregation of the fluorinated polymer blocks, Fig 8d. In addition, SEM top view of the modified cotton fabric shows that a layer of polymer was armored on the as-prepared superhydrophobic surface (Fig 8b).

In order for the polymer to anchor onto the cellulose materials covalent and hydrogen bonding were suggested. Samyn and coworkers (Samyn et al. 2011a; Stanssens et al. 2011) synthesized a block polymer with amide groups (Fig 9). The amide blocks exhibited good adhesion to the cellulose fibers, which was proposed to be the result of hydrogen bonding between the electronegative nitrogen in amide and the hydrogen of the hydroxyl groups in cellulose. The hydrophobic polystyrene blocks self-assembled outside of the fibers, rendering the system with low surface energy and nano-roughness.

Another method, admicellar polymerization, can be applied. It is a versatile method to form ultrathin polymeric films on a surface. This method consists of three main steps: Firstly, an admicelle in the form of a surfactant bilayer is formed on the substrate’s surface followed by the addition of an organic monomer that preferentially diffuses by its hydrophobicity into the hydrophobic core of the admicelle, a process called adsolubilization (Tragoonwichian et al. 2009). Finally, polymerization of the monomer in the admicelle is initiated through the addition of a suitable initiator such as ammonium persulfate. After the completion of the reaction, the weakly bound surfactants are washed away, leaving a thin polymer film coating on the surface. This method was employed by Tragoonwichian and coworkers to modify cellulose fibers (Tragoonwichian et al. 2009). The sodium salt of dodecylbenzenesulfonic acid (DBSA) was used as surfactant and first coated 2-hydroxy-4-acyrloyloxybenzophenone (HAB) on a cotton fabric. At last, methacryloxyethyltrimethyl-silane (MSi) was used to initiate the polymerization to form a thin layer. The structure of HAB and MSi is illustrated in Fig 10. In this work admicellar polymerization produced a bifunctional cotton fabric possessing both UV-protection and water-repellent property due to the UV adsorption of HAB and hydrophobicity of silane block. The resultant fabrics were found suitable for outdoor use where both UV-protection and water repellency are required, for example in coating materials and protective clothing.

Polyhedral oligomeric silsesquioxane (POSS) consisting of an inorganic silicon-oxygen cage with general composition SiO_{x} and organic substituents R capping the silicon atoms of the cage, were incorporated with fluorine-containing organic polymers to improve thermal and other properties of fibers (Gao et al. 2010; Wang et al. 2011a; 2013). Terpolymer of POSS, methyl methacrylate (MMA) and 2,3,3,3-tetrafluoro-2-(1,1,2,3,3,3-hexafluoro-2-(perfluoropropoxy) propoxy) propyl methacrylate [(HFPO)3MA] were synthesized successfully (Fig 11) to then coat cotton fabrics. The coated fibers possessed excellent water and oil repellency.
Fig 9. Imidization of poly(styrene-male anhydride) into poly(styrene-maleimide) in the presence of ammonium hydroxide (Samyn et al. 2011a).

Fig 10. Chemical structures of (a) 2-hydroxy-4-acryloyloxy-benzophenone (HAB) and (b) methacryloxymethyltrimethylsilane (MSt).

Fig 11. Preparation of P(POSS-MMA-(HFPOM3)a. Reprinted from (Gao et al. 2010) with permission from Elsevier.

Fig 12. FE-SEM images of POSS coated cotton fabrics surfaces. Insets are photos of liquid droplets on the corresponding samples: cotton fabric coated with P1 (a), cotton fabric coated with P2 (b), cotton fabric coated with P3 (c), cotton fabric coated with P4 (d). P1-P4 are terpolymers with increasing amount of POSS content. Reprinted from (Gao et al. 2010) with permission from Elsevier.

The WCA was observed to be a function of the POSS content. The contact angles were increased as the content of POSS in the terpolymer increased from 6.4 to 13.4 wt% from 140 to 152° and from 127 to 144°, in the case of water and natural oil, respectively. The super-hydrophobicity achieved by this POSS-based terpolymers may be due to the self-aggregation of the polymer chains grafted on the POSS cage. FE-SEM images of POSS and coated cotton fabrics surfaces are shown in Fig 12. It is clearly shown that with the increase of POSS (as indicated by P1, P2, P3 and P4 for increased POSS content), the nano-roughness generated by self-aggregation of the POSS-based terpolymers increased markedly. The insets provided in Fig 12 are images of liquid droplets on the corresponding samples.

In other efforts, electrostatic and van der Waals forces were utilized to adsorb polyelectrolytes on the surface of fibers. Lingström et al. (2007) treated individual wood fibers with polyelectrolyte multilayers consisting of two different polymer combinations, namely polyallylamine (PAH)/poly acrylic acid (PAA) (PAH/PAA) and polyethylene oxide (PEO)/PAA. They found that multilayer deposition not only increased the hydrophobicity but also the strength of paper made from the treated fibers. In this case, however, the treated fibers were not strictly superhydrophobic. This layer-by-layer (LbL) deposition method has been used by several other groups to create super-hydrophobic surfaces based on substrates different than lignocellulose (Ji et al. 2006).

Sol-gel process. The sol-gel process is a wet-chemical technique widely used in the fields of materials science. Such method is used primarily for the fabrication of materials (typically metal oxides) starting from a colloidal solution (sol) that acts as the precursor of an integrated network (gel) of either discrete particles or network polymers. Sol-gel processes have been used to produce super-hydrophobic surfaces from a variety of alkylsilane precursors, for example: tetraethoxysilane or tetraethyl orthosilicate (TEOS) (Ding et al. 2006; Huang et al. 2009; 2011b; Ivanova, Zaretskaya 2010; Latte et al. 2010), methyltriethoxysilane (MTEES) (Latte et al. 2010; Mahadik et al. 2010; Rao et al. 2010), tetramethoxysilane (TMOS) (Latte et al. 2009; Nadargi et al. 2010), methyl trimethoxy silane (MTMS) (Rao et al. 2006; 2009; Xu et al. 2011), methyltrichlorosilane (MTCS) (Shirgholami et al. 2011), trimethylchlorosilane (TMCS) (Rao et al. 2009), isobutyltrimethoxysilane (Xiu et al. 2008), phenyltrime-thoxysilane (Ph-TMS)(Rao et al. 2010), fluoroalkyl siloxane (Ivanova, Zaretskaya 2010) and sodium silicate (which is also called water glass) (Li et al. 2008b; Shang et al. 2010) and an industrial waterproof reagent [(potassium methyl silicate) (PMS)] (Li et al. 2008a), etc.

Taking the case of TEOS as an example, the sol-gel reactions of alkylsilane can be described by the following sequence (Bae et al. 2009)):

1) alkylsilane hydrolysis in acid or basic conditions:
   \[ \text{Si}-(OC\text{H}_3)_3 + 4\text{H}_2\text{O} \rightarrow \text{Si}-(\text{OH})_4 + 4\text{C}_2\text{H}_5\text{OH} \]

2) Alcohol condensation
   \[ \text{Si}-(\text{OH})_4 + \text{Si}-(\text{OC}\text{H}_3)_3 \rightarrow \text{Si}-(\text{O-Si})_2 + 4\text{C}_2\text{H}_5\text{OH} \]

3) Water condensation
   \[ \text{Si}-(\text{OH})_4 + \text{Si}-(\text{OH})_3 \rightarrow \text{Si}-(\text{O-Si})_2 + 4\text{H}_2\text{O} \]

Alkylsilane initially hydrolyze in acid or basic conditions to form silicic acid and then the formed silicic acid condensates with another alkylsilane or with itself to form a cross-linked polysiloxane network; thus, a gel is formed. The hydroxyl groups of polysiloxane can react with the hydroxyl group over the surface of a fiber and therefore the gel actually can be covalently attached to the fiber support.

In a similar way as that for TEOS, water glass and potassium methyl silicate can hydrolyze in the
presence of acid to produce silicic acid by the following reactions:

\[
\text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} + 2\text{H}^+ \rightarrow \text{Si}-(\text{OH})_3 + 2\text{Na}^+
\]

\[
\text{CH}_3\text{SiO}_3\text{K} + \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{CH}_3\text{Si}-(\text{OH})_3 + \text{K}^+
\]

The condensation reactions are the same as those discussed before in the case of TEOS. Some sol-gel precursors bear one or more organic chains, such as methyl, ethyl, phenyl and fluoroalkyl. These chemicals not only generate gel porous structures to render a nano-scale roughness but also introduce the respective low energy groups. In some reports two or more precursors are mixed to create roughness and reduce the surface energy via simple dip coating process (Rao et al. 2006; 2009; 2010; Xu et al. 2011). Post-treatment with long alkyl chains silanes is also reported. For example, Ding and coworkers (Ding et al. 2006; Miyauchi et al. 2006) modified electrospun hydrophilic cellulose acetate with a simple sol-gel coating of dodecyl(trimethoxy)silane (DTMS) and TEOS, as shown in Fig 13. Thus, sol-gel films were formed on the rough fibrous mats after immersion in the sol-gel. Through post-treatment of silane with low energy chains, a better surface hydrophobicity was obtained since the self-assembly of long hydrophobic chains on the surface formed aggregates that enhanced the nano-scale roughness. This sol-gel process can also be accomplished in a gas-solid reaction (Cunha et al. 2010b).

Cunha et al. (2010a) described a reactive precursor for sol-gel processes which contain a cyanate group. A precursor (3-isocyanatopropyl) triethoxysilane (ICPTEOS) reacted heterogeneously with the hydroxyl groups of cellulose in a DMF solvent. The reactions was followed by acid hydrolysis (and condensation) of the appended siloxane moieties as such, and in the presence of either tetraethoxysilane or 1H,1H,2H,2H-perfluoro-decyl-triethoxysilane. The reaction scheme is shown in Fig 14. Polycarboxylic acids were employed as cross-linker between cellulose fibers and silica coatings (Huang et al. 2011b; Liu et al. 2011). In contrast with inorganic acid and monocids, polycarboxylic acids act not only as catalyst in the preparation of the sol, but also as cross-linker between cellulose and the silica gel. It was observed that active hydrogen in citric acid remained after the hydrolysis reaction of water glass. This indicated the residual carboxylic acid groups in citric acid could continually react with hydroxyl groups of cellulose fibers to form ester bonds with sodium hypophosphite as the catalyst. The residual carboxylic acid groups could also react with Si–OH. The formed silica gel can be regarded as a structure with a polymer network cross-linked by citric acid groups. As a result, the compatibility and adhesion between the fiber surface and the silica sol as well as the hydrophobic durability are improved. It can be noted that residual hydroxyl groups in polysiloxane are readily reactive with the hydroxyl groups in cellulose; thus, the use of a crosslinker, e.g. cyanate, epox or polycarboxylic acid to bind cellulose and the silica layers is not necessary.

As far as the actual application, an interesting approach was presented by Taurino et al. (2008) who introduced an air-brush applicator to spray sol-gel solutions on given substrates. This method has the advantage of being simple and less expensive, compared to other conventional techniques. The air-brushing apparatus consists of a bottle with the sol-gel solution and an air-brush applicator (Fig 15). The morphology and surface energy of the coated surfaces can be adjusted by the air pressure and the precursors in the container. Sol-gel solution of TEOS, tetraethyl orthotitanate (TEOT), and tetra-n-propyl zirconate (TPOZ) mixed with α-o-tetraalkoxysilane-terminated PFPE were demonstrated to produce super-hydrophobicity on a variety of substrates with little or no pretreatment (Taurino et al. 2008).
In order to improve the bonding between silica coating and cellulose fibers, 3-glycidyloxypropyl-trimethoxysilane (GPTMS) was used as crosslinker (Shang et al. 2010). In their work, durable super-hydrophobic cellulose fabrics were prepared from water glass and n-octadecyltriethoxysilane (ODTES) and 3-glycidyloxypropyltrimethoxysilane (GPTMS) was used as crosslinker in the sol-gel method (cf. Fig 16). The result showed that the addition of GPTMS resulted in a better fixation of the silica coating from water glass on cellulose.

Deposition of nanoparticles on cellulosic surfaces. Some nanoparticles (NPs), such as those based on SiO₂, ZnO, CaCO₃ and TiO₂ can be applied to the surface of cellulosic substrates to produce roughness in the micro/nano scale. By using this method, post-treatment with fluorine-containing compounds (Xu et al. 2011; Yang, Deng 2008; Yu et al. 2007), silicones and functionalized organic materials can be used to reduce the surface energy and give super-hydrophobicity. This protocol is illustrated in Fig 17.

SiO₂ NPs. SiO₂ NPs are usually prepared using the Stöber method (Stöber et al. 1968). The principles to produce SiO₂ NPs are similar as those described in the sol-gel section. According to the mechanism of silane’s hydrolysis and condensation, the reaction time, catalyst and ratio of water/alcohol are primary factors to control the size of nanoparticles.

Silica NPs can attach onto cotton fibers by simple dip coating (Zhou et al. 2012), by spraying alcohol suspensions of SiO₂ nanoparticles (Oghara et al. 2012) or by heat treatment (Xu et al. 2011), resulting in the formation of a chemical bonds between hydroxyl groups of cellulose and silica. Thus, covalently attach to cellulose is produced without the requirement of binders. The surface of cellulose fiber carries negative charges in aqueous solution, and the NPs prepared are usually negatively charged as well. Therefore, the coverage of silica NPs on cotton fibers without treatment is quite poor (Bae et al. 2009; Yu et al. 2007), as shown in Fig 18a. In order to increase the coverage and also to enhance the roughness created by NPs, multilayers of silica NPs deposited from solution can be combined with cationic polyelectrolytes. For example, Yang and Deng (2008) developed a facile method for preparing a super-hydrophobic paper surface using multi-layer deposition of polydiallyldimethylammonium chloride (polyDADMAC) and silica particles, as shown in Fig 18b. Zhao et al. (2010) assembled multilayer by alternately immersing the treated fabric into 1.0 wt% aqueous solution of cationic poly(allylamine hydrochloride), PAH and a solution containing 1.0 wt% SiO₂ NPs. This electrostatic layer-by-layer (LbL) assembly is based on alternative adsorption
on charged substrates of oppositely charged poly-electrolytes, inorganic nanoparticles, macro-molecules or even supramolecular systems. It is a versatile technique to build up multilayered composite films in a controlled manner (Aulin et al. 2010a; Eita et al. 2012; Karabulut et al. 2012; Karabulut, Wågberg 2011; Tanaka, Ödberg 1992). Charged fibers are suitable as solid supports to conduct LbL since the assembly is independent of the size and topography of the substrates and uniform multilayers can be formed with different spatial structures. Fig 19 includes smooth surfaces and cotton fibers and the changes in the nano topography after application of coating layers.

Xue et al. (2009) developed another LbL protocol by modifying the surface of silica NPs with amino- and epoxy-functional groups, respectively. Alternate coating of amino- and epoxy-functionalized silica nanoparticles on epoxy-functionalized cotton textiles were used to generate a dual-size surface roughness, followed by hydrophobization (schematically illustrated in Fig 20) to produce super-hydrophobic surfaces. The static water contact angle of the most super-hydrophobic sample prepared reached 170°.

**ZnO nanorods (NRs).** ZnO NRs can be prepared on cellulose through a hydrothermal route. A seed layer of ZnO was obtained by solution-based (Xu, Cai 2008) and magnetron sputtering (Xu, Cai 2008; Lim et al. 2010) methods. In the solution method, zinc salt, zinc salt was dissolved in ethanol under vigorous stirring. Then a solution of hydroxide (0.15 M) in ethanol was slowly added and stirred. ZnO gradually deposited on the fibers and thus ZnO nanocrystals grew slowly on their surfaces. In the magnetron sputtering method, the substrate was treated by radio frequency magnetron sputtering (base pressure 10⁻³ mTorr, Argon plasma, rf power 100 W, working pressure 10 mTorr, deposition rate 12 nm/min). ZnO NRs were fabricated via a hydrothermal route with a growth solution containing an equimolar aqueous mixture of 25 mM zinc salt and hexamethylenetetramine and 0.1 g of poly(ethyleneimine) (PEI) (Xu, Cai 2008; Lim et al. 2010). The seeded layer-coated fabric was immersed in 50 ml of the growth solution contained in a glass bottle sealed with an auto-cleavable cap and heated at 90°C for 6 h. PEI was used to enhance the aspect ratio of the NRs. SEM images of ZnO NRs are included in Fig 21.

Compared with SiO₂ NPs, ZnO NRs have a much higher aspect ratio. Therefore, cellulose treated with ZnO NRs can yield lower roll-off angles and better water-repellent properties compared to SiO₂ NPs of similar diameter. This is due to the discontinuous three-phase contact line of NRs (Xu, Cai 2008).

**TiO₂ NPs.** TiO₂ is widely used in paper industry to produce better paper opacity (Farrokhpay 2009; Marques et al. 2006; Nelson, Deng 2008; Park et al. 2007). Nano-TiO₂ can improve significantly the brightness and opacity of paper materials because of its high index of refraction compared to cellulose fibers or other fillers. TiO₂ NPs were used to generate nano-roughness required for super-hydrophobicity as well (Xue et al. 2008). TiO₂ sol was prepared by a typical controlled hydrolysis process. For example, Xue et al. used a solution (Solution A) prepared by slow addition of 8.5 ml of tetrabutyltitanate into 20 ml of anhydrous ethanol under continuous stirring.

A second solution, Solution B, was prepared by mixing 1.5 ml of deionized water, 5 ml of acetic acid, and 20 ml of anhydrous ethanol together with stirring. Upon slow addition (1 h) of Solution A into Solution B the reaction mixture was stirred for 24 h at room temperature and as a result, a transparent bright yellowish TiO₂ sol was obtained (Xue et al. 2008). The as-prepared TiO₂ NPs was applied to cellulose to increase its roughness. Hydrophobization was needed in order to lower the surface energy of the TiO₂-coated substrate.

Due to the extremely large surface area-to-particle size ratio, nanosized-TiO₂ pigments were poorly retained when mechanically mixed with fibers. Thus, Huang and coworkers (Huang et al. 2011a) reported a type of paper with super-hydrophobic and photocatalytic properties after modification with TiO₂ NPs and a silane molecule, 3-(trimethoxysilyl)propyl methacrylate (MPS). MPS-modified nano-TiO₂ particles were added to the fiber suspension before the process of beating to inhibit agglomeration of TiO₂ on the surface of the fibers.

Kettunen et al. (2011) used a chemical vapor deposition method to coat a thin TiO₂ film on lightweight native nanocellulose aerogels to offer a novel type of functional material that shows photo-switching between water-superabsorbent and water-repellent states. Highly porous, nanocellulose aerogels were here first formed by freeze-drying from the corresponding aqueous gels (Jin et al. 2011). In this straightforward, one-step process the nanocellulose aerogels were exposed to titanium isopropoxide vapor at 190°C at pressures of 1–5 kPa for 2 h. Well-defined, nearly conformal TiO₂ coatings with thicknesses of ca. 7 nm were obtained.

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Fig 19. SEM images of untreated cotton fabric (a and b) and cotton fabrics assembled with (PAH/SiO₂)n multilayers: n = 1 (c), n = 3 (d), n = 5 (e), and n=7 (f). Reprinted from (Zhao et al. 2010) with permission from Elsevier.
The LbL method was employed to deposit TiO$_2$/poly(acrylic acid) (PAA) on fiber surfaces in order to increase the coverage of TiO$_2$ NPs and the roughness of the cellulose fibers (Li et al. 2010b; Ogawa et al. 2007). The process included hydrophobization with long chain silane molecules (Li et al. 2010b).

**Liquid flame spray (LFS)** coating is a technique which generates NPs and can be used to simultaneously coat substrates (Stepien et al. 2011; Teisala et al. 2010). A LFS setup is schematically illustrated in Fig 22.

In the LFS process the precursor fluids diluted in water or alcohol are fed together with the combustion gases into a specially designed spray gun. Instantly after exiting the burner nozzle the precursor solution is atomized to micron-sized droplets by the high-velocity gas flow. Liquid droplets evaporate in a hot and turbulent flame and subsequent reactions of the precursor vapor lead to formation of NPs of desired material. Afterwards the NPs grow larger in the flame by condensation, coagulation, coalescence and agglomeration. The final particle size can be controlled, e.g. via total mass flow rate of the precursor (product of the precursor solution feed rate and its concentration) or by adjusting the collecting or depositing distance. The main exhaust gases formed as by-products in the LFS process are normally water vapor and carbon dioxide. Low waste flows combined with relatively simple and inexpensive equipment make the LFS process comparatively cheap and environmentally friendly.

The major advantage of such process is the broad spectrum of metal or metal oxide NPs that can be created using different liquid precursors. For example, Stepien et al (2011) dissolved titanium (IV) isopropoxide (TTIP) or tetraethylorthosilicate (TEOS) precursor in isopropanol (IPA) to adjust the wetting properties of paperboard with nanosized TiO$_x$ or SiO$_x$ coatings produced by the LFS process. SEM images of TiO$_x$ or SiO$_x$ coated paperboard were shown in Fig 23.

**Ag NPs.** Silver and silver ions have been reported to be effective against nearly 650 trends of bacteria (Dubas et al. 2006) due to their ability to attach to the their cell membranes, penetrate and attack the respiratory chain of the cell, hence leading to the bacteria’s death (Morones et al. 2005; Rai et al. 2009). Silver NPs (Ag NPs) appear to exhibit enhanced antibacterial activity due to their increased surface area, which provides larger contact possibilities with microorganisms per surface unit. In addition, Ag NPs are also known to release silver ions thereby enhancing their bactericidal activity (Morones et al. 2005; Rai et al. 2009). Ag NPs have been incorporated onto various polymeric fibers and the resultant fibrous composites have reported successful antibacterial activity.
Generally, there are two methods to deposit Ag NPs onto polymeric fibers. The first method consists of preparing colloidal Ag NPs by reducing Ag salts, e.g. AgNO₃, using reducing agents such as NaBH₄, citrate or sugars. This synthesis is commonly followed by immersion of fibers into the colloidal Ag NP solution hence directly depositing the NPs onto the fiber’s surface through electrostatic interactions (Dong, Hinestroza 2009), hydrogen bonding (Dong et al. 2008), or through a layer-by-layer deposition (Duhas et al. 2006). An alternative route is an in situ method, where Ag ions are initially adsorbed onto fiber surfaces and then post-treated with UV radiation (Chen, Chiang 2008), heat treatments (Ifuku et al. 2009), chemical reduction (Dong, Hinestroza 2009), ultrasound (Perelshtein et al. 2008) or microwave (Chen et al. 2008) to reduce Ag ions into Ag NPs.

Besides the production of antibacterial fabrics, Ag NPs can be used as a facile and effective method to prepare super-hydrophobic cellulose (Khalil-Abad, Yazdanshenas 2010). For example, Ag NPs were produced on cotton fibers by treatment with aqueous KOH and AgNO₃, followed by reduction treatment with ascorbic acid in the presence of a polymeric steric stabilizer, generating a dual-size surface roughness. Further modification of particle-containing cotton textiles with octyltriethoxysilane (OTES) led to hydrophobic surfaces. The procedures are schematically illustrated in Fig 24 while SEM images of Ag NPs coated fabric are presented in Fig 25.

The surfaces prepared showed a sticky hydrophobicity: a static water contact angle of 151° was measured for a 10 μl droplet of water that did not slide off even when the sample was held upside down. The modified cotton was found to have potent antibacterial activity toward both Gram-positive and Gram-negative bacteria.

**CaCO₃ NPs.** CaCO₃ is a mineral which is widely used in the paper industry. CaCO₃ NPs can be prepared by the reaction of sodium carbonate with calcium chloride in the presence of oleic acid and heptadecafluorodecyltrimethoxysilane (Wang et al. 2010) or obtained from commercial precipitated calcium carbonate (PCC) particles (Hu et al. 2009). The advantages of CaCO₃ include its low cost and nontoxicity. Hu et al. (2009) used a polymer latex agent as polymer binder in order to increase the adhesion of CaCO₃ NPs to cellulose fibers. Commercial PCC, hydrophobic stearic acid and polymer latex particles were used for surface roughness control, surface hydrophobic modification agent, and polymer binder, respectively. A simple coating via dipping was used to produce papers with high WCA and water resistance. It was found that the surface pretreatment of PCC with fatty acid salt prior mixing with polymer binder played an important role for improving the WCA. The combination of surface coating with dipping treatment further increased the WCA and water resistance of the paper. A WCA near 150° over modified paper surface was achieved. The morphology of the surface of the paper coated using modified PCC with different polymer content can be observed in Fig 26 as a function of latex content.

**Organic NPs.** Organic NPs have also been used to create the required nano-roughness and low surface energy. The literature available that addresses cellulose substrates is very limited, though. Quan et al. utilized alkyl ketene dimer (AKD) NPs, which were generated from rapid expansion of supercritical solutions (RESS) to produce super-hydrophobic cellulose fibers (Quan et al. 2009). AKD is a common sizing agent used in the paper industry (Asakura et al. 2006; Lindfors et al. 2007; Lindström, Glad-Nordmark 2007a; b; Lindström, Larsson 2008; Ohga et al. 2008) and is a crystallizing wax with a melting point between 40 and 60°C, depending on the dimer carbon chain length (see the chemical structure of AKD in Fig 27). AKD acts by increasing the contact angle of the fibers to levels of around 110°. The RESS process utilizes the high solvating power of supercritical carbon dioxide (SC-CO₂) to make fine (nano to micron-sized) particles.
After dissolving the AKD in SC-CO$_2$, an extremely fast phase transfer from the supercritical to the gas-like state takes place during the expansion into atmospheric condition. Because of the high super-saturation in SC-CO$_2$, extremely small particles can be formed in the RESS process (Quan et al. 2009; Werner et al. 2010). One advantage of the RESS process is the ability to produce solvent-free products without the need for additional solvents or surfactants to induce precipitation. Since the solvent is a dilute gas after expansion, the RESS process offers a highly pure final product that enable a much more convenient way in making super-hydrophobic paper or other solid substrates.

Finally, electro-spinning, which is normally used to produce nanofibers, can be used to spray polymer solutions onto a substrate to generate micro/nano particles, as in electrospaying. Electrospinning cellulose fibers will be covered in later sections. Sarkar and coworkers (2010) employed this technique to electro-spray polyvinylidene fluoride and fluorinated silane molecules onto cellulose materials (cotton fabric or paper) with different concentrations for differential super-hydrophobicity and hydrophilicity on each side of the surfaces. They found that a smaller particle diameter enhanced super-hydrophobicity when a constant surface roughness and surface chemical composition were used.

Chemical vapor deposition (CVD). Chemical vapor deposition (CVD) is a chemical reaction which transforms gaseous molecules, called precursor, into a solid material, in the form of thin film or powder, on the surface of a substrate (Alf et al. 2010; Asatekin et al. 2010). The CVD approach is regarded as a simple and effective method to deposit super-hydrophobic coatings onto substrates. For vapor deposition, the reaction temperature in the chamber is required to be higher than the boiling point of the precursor. For example, silane precursors of trichloromethylsilane (TCMS) and dimethyl-dichlorosilane (DMDCS) require a temperature higher or close to the boiling point of the precursor, 66°C, and 68–70°C, respectively (Li et al. 2007; Oh et al. 2011). Cotton fabrics or filter papers were placed in a sealed chamber for a set time, into which a vapor of precursor was introduced. The precursor was absorbed onto the cotton fibers’ surface and penetrated into the fibers and reaction between the halide and hydroxyl groups took place. An efficient reaction enhanced the content of covalently bound silicone to the fibers’ surfaces. After the deposition, condensation of silane polymers was required. This step was conducted in an aqueous solution of pyridine (1 M) at room temperature to hydrolyze the remaining Si–Cl bonds (Li et al. 2007). Finally, subsequent polymerization of Si–OH was accomplished in an oven at 150°C for 10 min, which resulted in a nano-scaled silicone coating tightly attached to the surface. Therefore, this method can be regarded as a special sol-gel process in which the precursor attaches to the surface in gaseous phase rather than in solution. One disadvantage of this process is that the wet tensile strength can be reduced, which is caused by the generation of hydrogen chloride during reaction that degrades the acid-sensitive cellulose fibers (Oh et al. 2011).

Laser assisted chemical vapor deposition. Chemical vapor deposition is the simplest method for deposition and has the advantage of easy controllability. However, one drawback of chemical vapor deposition is that the polymer used has to be readily vaporized. Pulsed Laser Deposition (PLD) enables the deposition of materials with high melting point.

PLD is a dry process, very versatile and has several advantages in the formation of thin films of functional materials. The schematic of PLD is observed in Fig 28a. A laser is utilized as energy source to evaporate a target material that is placed on a carousel. The laser plume deposits onto the surface of the substrate which is placed on the sample stage. Through PLD, it is possible to control the film thickness digitally at the angstrom-scale. It is also possible to deposit a hetero-structure or multi-layer film whose structure differs from layer to layer by changing the ablation target appropriately. Among available organic materials, polytetrafluoroethylene (PTFE) has been the main target in PLD because it exhibits poor solubility in all solvents and has low surface adhesion. Note that conventional wet processes such as spin-coating methods are not applicable for the formation of thin PTFE films. Daoud et al. (2006) used PLD to deposit a uniform 50-70 nm layer PTFE on cellulose cotton substrates and achieved a WCA of 151°. The morphology of fiber surface is shown in Fig 28b-c to illustrate the effect of such nano deposition.
Plasma assisted chemical vapor etching and deposition. Plasma-based technologies are exciting alternatives for cellulose and paper modification. Plasma is ionized gas consisting of a mixture of free electrons, ions and neutral atoms (depending on the degree of ionization) and is formed when sufficient energy is put into a gas. Under laboratory conditions, ionized gas is generated by using high electric fields, known as cold plasma or electric discharge. Ionized molecules with high energy can be bombarded on the surface of a given substrate. Most of the chemistry occurs on the surfaces within the reactor due to the high energy ion bombardment. High energy ions cause relatively unselective fragmentation of the surface adsorbed species and a deposition or etching processes results, depending on the power and molecules involved (Tendoro et al. 2006).

Through plasma-assisted CVD technique, physical heterogeneities (roughness) of fibers can be minimized by selective etching of the amorphous cellulose domains in oxygen plasma (Balu et al. 2009). The low surface energy of these etched paper surfaces can be obtained by depositing a thin film of perfluorothane (PFE) (Balu et al. 2008; 2009) or fluorotritylmethane (FTMS) (Navarro et al. 2003; Vilaseca et al. 2005) from the plasma environment.

Atomic layer deposition (ALD) technique, similar with CVD, is a chemical process to deposit a thin layer or film by sequential use of a gas. Al₂O₃ and SiO₂ coatings deposited on cellulose-base materials have been reported to function as gas and vapor barriers (Hirvikorpi et al. 2010; 2011a; 2011b; 2011c). Cotton fibers were modified with ZnO to make them conductive (Jur et al. 2011). In the ALD process, a metal organic precursor (e.g. bis(diethyldiamino) silane, trimethylaluminium and diethyl zinc) and a reactant (e.g. water) are sequentially exposed to a surface desired to be modified, resulting in a complementary sequence of self-limiting reactions. ALD allows preparation of dense and pinhole-free inorganic films. ALD is expected to be a promising method to produce super-hydrophobic surfaces with topography control.

Roughness offered by regeneration of cellulosic materials, cellulose nanocrystals and composites

The previous section dealing with chemical grafting, nanoparticle deposition and chemical vapor deposition, introduced the roughness required to attain super-hydrophobicity, by self-assembled polymer, nanoparticles etc. In this section, the roughness required for super-hydrophobicity is produced by the cellulosic material itself, i.e., by regeneration or nanofibrillation. These techniques include electrospinning and electro-spraying and application of cellulose nanocrystals and aerogels.

Electrospinning. In electrospinning, high voltage, typically 5-30 kV, is applied between a spinnere(s) and a collector, and therefore a static electric field is established between. A so-called Taylor cone forms due to the competing forces of the static electric field and the liquid’s surface tension. For liquids with a finite conductivity, charged droplets are dispersed from the tip of the Taylor cone and are delivered to the target. If the liquid consists of a polymer melt or a polymer solution and the concentration of that polymer is sufficiently high to cause molecular chain entanglement, a fiber, rather than a droplet, is drawn from the tip of the Taylor cone (Huang et al. 2003; Li, Xia 2004).

Electrospinning of cellulose has been extremely challenging because of its high crystallinity, which prevents its dissolution in common solvents. Manufacturing of electrospin cellulose fibers has been reported through direct electrospinning of cellulose solution in N-methylmorpholine-N-oxide (NMMO) hydrate (Kim et al. 2006), lithium chloride (LiCl)/N, N-dimethyl acetamide (DMAc) (Kim et al. 2005; 2006), Urea/NaOH solution (Qi et al. 2010) and ionic liquids (Quan et al. 2010; Viswanathan et al. 2006). However, cellulose solutions of NMMO or LiCl/DMAc must be electrospun at elevated temperatures and all three resulting cellulose fibers require post-treatment with water in order to completely remove residual solvents. An alternative approach to the direct electrospinning of cellulose derivatives solution which is easy to dissolve, for example cellulose acetate (CA)(Han et al. 2008; Liu and Hsieh 2002; Son et al. 2004a; b; Vallejos et al.). CA can be electrospun in a mixture of acetone/water or methylene chloride/ethanol (Han et al. 2008; Liu, Hsieh 2002; Yoon et al. 2009; Son et al. 2004a; b; Song et al. 2012).

Binary roughness can be fabricated through electrospinning. Micro/nano roughness can be achieved by the entanglement of electrospin fiber in the mat. In addition, nano pores can be created during electrospinning due to the rapid solvent evaporation. Furthermore, the pore structure can be adjusted by altering the ratio of methylene chloride/ethanol as reported by Yoon et al. (Yoon et al. 2009). Fig 29 demonstrates the micro fiber and nano porous structure as a function of ratio of methylene chloride/ethanol. Super-hydrophobic electrospin CA mat have been achieved by treating the fibers with a CF₃ plasma (Yoon et al. 2009).

Cellulose composites. Fine solid particles such as silica, carbon black, and clay when adsorbed at liquid-liquid interfaces can act as stabilizers for emulsions, foams, and water droplets replacing surfactants. Emulsions stabilized with such surface active particles are called “Pickering emulsions”. Bayer et al. (2009) utilized related approaches to fabricate nano-rough cellulose surfaces. Emulsions were formed by dispersing cyclosiloxanes in water stabilized by layered silicate particles and were subsequently modified by blending into a zinc oxide nano fluid. The polymer matrix was a blend of cellulose nitrate and fluorocrylic polymer pre-compatible in solution. Coatings were sprayed cast onto substrates from polymer blends dispersed in modified Pickering emulsions. As a result, super-hydrophobic cellulose-based biocomposite films were formed without post-treatment.

Cellulose nanocrystals and nanofibrillated cellulose. Cellulose nanocrystals (CNC) (Rányby 1949; 1951, Rányby, Ribi 1950,) are prepared by removing the amorphous domains and keeping the crystalline regions of cellulose (Beck-Candanedo et al. 2005; Cranston, Gray 2006; Edgar, Gray 2003; Fu et al. 2012; Habibi et al. 2010; Moon et al. 2011). Aulin et al. (2009) took advantage of the nano-size and properties of cellulose nanocrystals to
produce super-hydrophobic surfaces by assembling multilayers of poly(ethyleneimine) (PEI) and colloidal CNCs followed by hydrophobization with (tridecafluoro-1,1,2,2-tetrahydrooctyl-)trichloro-silane in heptane solution.

Micro- or nanofibrillated cellulose (NFC), another form of nanocellulose (Turbak 1983) can be isolated through high-shear mechanical disintegration and homogenization of cellulose fibers (Adhelgawad et al. 2013; Ferrer et al. 2012a; Henriksson et al. 2008; Spence et al. 2010a; 2010b; Zimmermann et al. 2010; Zimmermann et al. 2004). Porous aerogels of NFC were prepared by freeze-drying (cf. Fig 30) followed by chemical vapor deposition with 1H,1H,2H,2H-perfluorodecyl-trichlorosilane (PFOTS) which was used to uniformly coat the aerogel and to tune their wetting properties towards non-polar liquids (Jin et al. 2011; Aulin et al. 2010b) or by functionalizing the native cellulose nanofibrils of the aerogel with a hydrophobic but oleophilic titanium dioxide to produce floating, sustainable, reusable, and recyclable oil absorbents (Korhonen et al. 2011). Recent work by Mertaniemi et al. reported using air-brush techniques with solvent-based NFC onto the surface, followed by quick drying, and a chemical modification performed either before or after the airbrushing, to produce super-hydrophobic surfaces (Mertaniemi et al. 2012).

Contact angle hysteresis of cellulose-based superhydrophobic surfaces

For self-cleaning applications a low sliding angle or low contact angle hysteresis is an important requirement. Therefore, any wetting analysis requires the determination of both the advancing and receding contact angles, as was defined in previous sections of this review. Unfortunately, many reports in the literature only consider a single, “static” contact angle. A convenient way to quantify related phenomena is simply performed by calculating the difference between the advancing and receding contact angles, i.e., the contact angle hysteresis.

Thus, reducing the water contact angle (WCA) hysteresis is effective toward reducing water adhesion to the surface and promoting self-cleaning ability (Chen et al. 1999; Wier et al. 2006). Table 1 includes a compilation of values of WCA hysteresis reported in the literature for various cellulose-based substrates. It also includes there respective static WCA and the material used to induce roughness on the surface as well as the respective strategy used to lower its surface energy. A wide range of contact angle hysteresis values exist even if a very high static WCA is achieved. In most cases, a very small contact angle hysteresis (<5°) is observed; however, in some cases, relatively large WCA hysteresis are noted: 13-20° for cellulose fabrics coated with silica nanoparticles followed by modification with hexadecyl-trimethoxysilane (Xu et al. 2011) or 14-35° if methyl-trichlorosilane is used (Shirgholami et al. 2011). Even higher hysteresis was measured in cases where the substrate was coated with polymer NPs (>50° or as high as 112°) (Samyn et al. 2011a; Stanssens et al. 2011). An interesting case is that of layer-by-layer deposition of silica NPs on cotton fibers followed by treatment with fluoroalkylsilane. In such cases the WCA were above 150°, while the hysteresis angle varied with the deposition layers: for 1 or 3 layers, the fabrics showed adhesive contact with the water drop and a high contact angle hysteresis (>45°). Systems with 5 layers or more, produced slippery super-hydrophobicity, with a contact angle hysteresis lower than 10° (Zhao et al. 2010). The greatest hysteresis angle was achieved in the case of cellulose coated with Ag NPs and treated with octyl-trithoxysilane; in this case the water drop also exhibit adhesive contact with the substrate, even if it was hold upside down.

WCA hysteresis is affected by the substrate, its roughness and texture and the coating material as well as the strategies used to change the surface energy of the system. However, contact angle hysteresis and adhesive hydrophobicity is a subject still not fully understood (Chen et al. 1999; Gao, McCarthy 2006; Wier et al. 2006). To complicate matters, poorly covered cellulose substrates are often difficult in accurate measurements of WCA and hysteresis (Xu, Cai 2008; Khalil-Abad, Yazdanshenas 2010).
Table 1. Static water contact angle (SWCA) and WCA hysteresis as reported for different cellulose-based substrates upon roughness and surface energy modification with different nanoparticles (NPs) and/or surface treatments.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Roughness</th>
<th>Surface energy</th>
<th>SWCA</th>
<th>Hysteresis</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>Ag NPs</td>
<td>Octyltriethoxysilane</td>
<td>139-151</td>
<td>did not slide off</td>
<td>(Khalil-Abad, Yazdanshenas 2010)</td>
</tr>
<tr>
<td>Cotton</td>
<td>Amiphilic fluorinated triblock azide</td>
<td>copolymers</td>
<td>155</td>
<td>&lt;5</td>
<td>(Li et al. 2010b)</td>
</tr>
<tr>
<td>Cellulose</td>
<td>‘graft-on-graft’ architecture</td>
<td>Fluorinated end brushes</td>
<td>170</td>
<td>Very small, once tilted</td>
<td>(Nyström et al. 2006)</td>
</tr>
<tr>
<td>Paper</td>
<td>Polymer NPs</td>
<td>Polymer</td>
<td>100-120</td>
<td>82-112</td>
<td>(Samyn et al. 2011a)</td>
</tr>
<tr>
<td>Paper</td>
<td>Polymer NPs</td>
<td>Polymer</td>
<td>79-120</td>
<td>50-98</td>
<td>(Stanssens et al. 2011)</td>
</tr>
<tr>
<td>Cotton fabrics</td>
<td>POSS</td>
<td>Fluorinated end brushes</td>
<td>Up to 152</td>
<td>4-7</td>
<td>(Gao et al. 2010)</td>
</tr>
<tr>
<td>Silica NPs</td>
<td>Stearic acid/ perfluorodecyltrichlorosilane</td>
<td>Up to 150</td>
<td>&gt;150</td>
<td>&gt;45 (1-3 layers); ~5 (above 5 layers)</td>
<td>(Zhao et al. 2010)</td>
</tr>
<tr>
<td>Silica NPs</td>
<td>Hexadecyltrimethoxy-silane</td>
<td>Up to 150</td>
<td>13-20</td>
<td>(Xu et al. 2011)</td>
<td></td>
</tr>
<tr>
<td>Wood fiber</td>
<td>Silica NPs</td>
<td>Fluoroalkylsilane</td>
<td>&gt;150</td>
<td>&lt;5</td>
<td>(Yang, Deng 2008)</td>
</tr>
<tr>
<td>cotton fibers</td>
<td>LbL Silica NPs</td>
<td>Fluoroalkylsilane</td>
<td>&gt;150</td>
<td>&gt;45 (1-3 layers); ~5 (above 5 layers)</td>
<td>(Zhao et al. 2010)</td>
</tr>
<tr>
<td>Cotton textiles</td>
<td>Porous silica</td>
<td>Methyltrichlorosilane</td>
<td>145-170</td>
<td>14-35</td>
<td>(Shirgholami et al. 2011)</td>
</tr>
<tr>
<td>Paper</td>
<td>RESS</td>
<td>AKD</td>
<td>Up to 173</td>
<td>Very small, once it tilted</td>
<td>(Quan et al. 2009)</td>
</tr>
<tr>
<td>Cotton fabric or paper</td>
<td>electro-spraying</td>
<td>Polyvinylidene fluoride and fluorinated silane</td>
<td>~160</td>
<td>5-6</td>
<td>(Sarkar et al. 2010)</td>
</tr>
<tr>
<td>Pulp fiber</td>
<td>TiO2 NPs</td>
<td>3-(trimethoxysilyl) propyl methacrylate</td>
<td>Up to 154.2</td>
<td>~3</td>
<td>(Huang et al. 2011a)</td>
</tr>
<tr>
<td>Cotton fabrics</td>
<td>ZnO NPs</td>
<td>n-dodecyltrimethoxysilane</td>
<td>~161</td>
<td>9</td>
<td>(Xu, Cai 2008)</td>
</tr>
<tr>
<td>Cotton fabrics</td>
<td>SiO2 NPs</td>
<td>n-dodecyltrimethoxysilane</td>
<td>159</td>
<td>29</td>
<td>(Xu et al. 2010)</td>
</tr>
<tr>
<td>Cotton fabrics</td>
<td>ZnO NPs</td>
<td>n-dodecyltrimethoxysilane</td>
<td>153</td>
<td>9</td>
<td>(Xu et al. 2010)</td>
</tr>
</tbody>
</table>

**Durability of super-hydrophobic cellulose**

Due to the high surface roughness required to endow materials with super-hydrophobicity, the respective surfaces are generally easily damaged by scratching or erosion. In nature, a damaged surface can be repaired by regenerative processes (Genzer, Efimenko 2006). However, synthetic super-hydrophobic surfaces, bio-inspired or not, are not easily repaired from damage. Techniques such as wet chemical procedures may be difficult to apply in order to repair damaged roughness and surface chemistry. Spray and chemical vapor deposition may have advantages over wet chemical procedures as they are easy to apply in order to recover the required roughness and low surface energy (Basu, Paranthaman 2009; Verho et al. 2011). Mechanical durability offered by hierarchical roughness ensures that stable Cassie state remains even after some surface features are worn away. Such morphology involves robust micro-scale bumps that provide protection to a more fragile nano scale roughness that is superimposed on the larger pattern (Verho et al. 2011).

A number of applications involve surfaces that are subject to different degrees to abrasive forces, for example, outdoor facades or window panes, solar panels, liquid handling devices used in microfluidics, etc. The interaction between super-hydrophobic surface and water is a key factor influencing most of the application (Zimmermann et al. 2007). Compared with other synthetic or inorganic superhydrophobic surfaces, super-hydrophobic surfaces based on lignocellulose may have some disadvantage as far as the chemical stability due to its inherent hydrophilicity.

The chemical durability of superhydrophobic cotton was evaluated by washing and abrasion (Wang et al. 2013; Zhou et al. 2012). Based on their experiment, the coated fabric that incorporate fluorinated decyl-polyhedral oligomeric silsesquioxane (FD-POSS) and fluorinated alkyl silane into the poly(3,4-ethylenedioxythiophene) (PEDOT) layer could withstand at least 500 cycles of standard laundry and 10 000 cycles of abrasion without apparently changing the super-hydrophobicity. In another experiment, the PD-POSS was substituted with silica nanoparticles. The coated fabrics withstand at least 600 cycles of standard laundry and 8000 cycles of abrasion.
abrasion without apparently changing the super-hydrophobicity.

The chemical durability of super-hydrophobic cotton fabrics varies with pH of media. Fig 3I demonstrates that the change of WCA against immersion time in aqueous solutions with different pH by Li et al. (Li et al. 2008a). The super-hydrophobic features involved the assembly of a precursor silanol (potassium methyl silicate, PMS) film on the cellulose surface and then polycondensation of the (PMS) aqueous solution with CO₂ at room temperature. The resultant super-hydrophobic cellulose showed satisfactory durability in acidic and neutral condition but less in basic medium.

There is an expanding range of applications of super-hydrophobic cellulose materials as described in sections 3.1 and 3.2. In addition, a number of super-hydrophobic surfaces which can be produced from cellulose substrates have been reported by using different methods. How the surface chemistry and the topography influence the stability of super-hydrophobic lignocellulosic surfaces is still a key issue that deserves further attention. In this regards, some topics that are to be considered in order to control the durability of super-hydrophobic behaviors include the impact on surface energy of end groups, cross-linking agents, functional group and inorganic nanoparticle density, as well as the thickness of coated layers, etc.

Final remarks

Even through know-how in the development of super-hydrophobic cellulose-based materials has undergone a rapid progress and has attracted considerable attention in recent years, robust and inexpensive methods are still in their infancy; in addition, a number of questions need to be addressed which require further research. Firstly, there is deficient information on the effect of lignin and heteropolysaccharides in the development of super-hydrophobic materials. Lignin and heteropolysaccharides present in the cell wall of wood fibers make up an important fraction of their composition. Compared with the polysaccharide components, lignin has a lower polar surface energy and a lower dispersive surface energy and therefore if it is used in the fabrication of super-hydrophobic materials, the demand for chemicals with low surface energy may be reduced. In addition, environmental pressures and more efficient resource utilization may stimulate more widespread use of residual lignocellulose (Ferrer et al. 2012b). Ionic liquids have been used to dissolve whole wood (Fort et al. 2007; Xie, Shi 2006). However, the high cost and the difficult recovery of ionic liquids may hinder its large-scaled application.

The costs involved in the fabrication of super-hydrophobic materials based in cellulose are also an issue. As a matter of fact, very limited reports exist on successful large-scale production of super-hydrophobic materials from cellulose. It is proposed that well-established textile and papermaking processing may be utilized in the production of cellulose-based super-hydrophobic materials. In such case, one can envision a major shift in material base and industry in the bio-economy of the future.

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