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REVIEW

Hydrophilic and superhydrophilic surfaces and materials

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The term *superhydrophilicity* is only 11–12 years old and was introduced just after the explosion of research on *superhydrophobic* surfaces, in response to the demand for surfaces and coatings with exceptionally strong affinity to water. The definition of superhydrophilic substrates has not been clarified yet, and unrestricted use of this term to hydrophilic surfaces has stirred controversy in the last few years in the surface chemistry community. In this review, we take a close look into major definitions of hydrophilic surfaces used in the past, before we review the physics behind the superhydrophilic phenomenon and make recommendation on defining superhydrophilic surfaces and coatings. We also review chemical and physical methods used in the fabrication of substrates on surfaces of which water spreads completely. Several applications of superhydrophilic surfaces, including examples from the authors' own research, conclude this review.

1. Introduction

The interest in manipulating hydrophilicity and hydrophobicity of solid surfaces and producing coatings with either strong or poor affinity to water exploded in the last twenty years, especially after a wide acceptance that liquid spreading control can simply be accomplished through changes in surface roughness and topography. *Superhydrophobicity*, *superhydrophilicity*, and *superwetting* are now the most popular topics in wetting studies with many research groups attempting to understand and reveal the physics behind liquid penetrating (or suspending on) the surfaces of complex geometries and structures, often controlled at the sub-microscopic level. The fundamentals of superhydrophobicity, fabrication of water-repelling surfaces and

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Emil Chibowski

Emil Julian Chibowski: born in 1943 in Poland. 1962–1967 studied chemistry at Maria Curie-Sklodowska University, Lublin, Poland where obtained MSc. Since 1967 employed at the Department of Physical Chemistry, at the same University, where in 1973 obtained PhD, in 1981 DSc, and in 1989 the title of Professor of Chemistry. Since 1993 head of the Department of Physical Chemistry. 1988–1989 post doc at Baylor University, Waco, TX; 1991–1992 sabbatical at Granada University; 2000–2001 visiting professor at Jaen University, both in Spain. Fields of interest: interfacial phenomena, wetting, surface free energy, electrokinetic phenomena, effect of magnetic field on the dispersed systems. Published over 200 papers. Cited >1600 times, H*-index = 17.*

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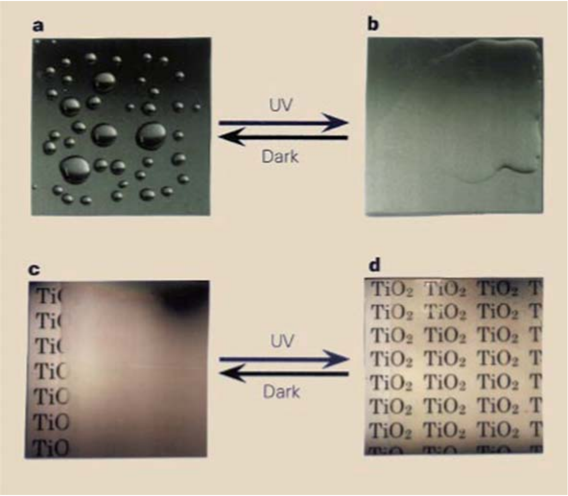

Fig. 1 Effect of UV radiation on hydrophilicity and transparency of a glass slide coated with a TiO_2 thin film. Water remains in the shape of lenses with a contact angle of 70–80° on the TiO_2-coated glass when stored in dark (a and c), but spreads completely when exposed to UV radiation (b and d) (reprinted from ref. 18 with permission).

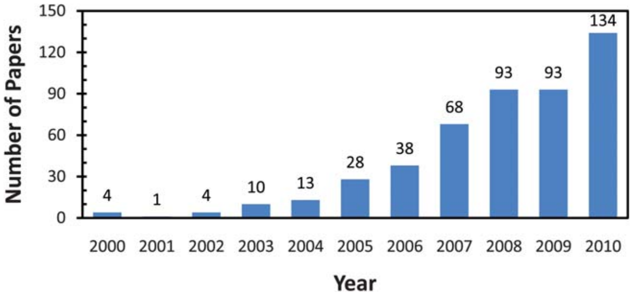

Fig. 2 Number of papers published in each year between 2000 and 2010 in which terms superhydrophilicity and/or superhydrophilic were used, according to the ISI Web of Knowledge scientific base search.

coatings and their applications were reviewed by several authors on a number of occasions since 2005.[1–15] However, there has been no extensive review of research on superhydrophilic surfaces, and this paper intends to fill this gap.

The terms "*hydrophilic surface*" and "*hydrophobic surface*" have been used in the literature for many decades and they are commonly used to describe incongruous behavior of water on a solid surface. A hydrophilic surface has a strong affinity to water whereas a hydrophobic surface repels water. This simple definition, however, is too general for the classification of a variety of different solids having different wetting characteristics, typically studied in three-phase systems with water and air or water and oil as fluids. Surprisingly, a variety of different definitions of hydrophilic and hydrophobic surfaces are used by the diverse scientific community. We found it important to briefly review the most common definitions in this paper.

The roots of the term superhydrophilicity date back to 1996, when Onda *et al.*[16,17] published two highly cited papers on the wettability of fractal (rough) surfaces in which the terms superhydrophobic and superwetting surfaces were proposed. Then in 1997 Fujishima *et al.*[18] demonstrated a superhydrophilic effect on a glass slide coated with a thin TiO_2 polycrystalline film (Fig. 1). Although the spreading of water was the result of both hydrophilic properties of anatase exposed to UV radiation and submicroscopic roughness of the coating, the effect of water spreading was entirely attributed to the photoinduced self-cleaning capability of TiO_2 at that time and the term superhydrophilicity was not used. The term appeared for the first time in the technical literature in 2000, in four papers published by three different research groups from Japan.[19–22]

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Konrad Terpilowski

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Since 2000, the number of papers published on the preparation of superhydrophilic surfaces and coatings persistently increases every year. Fig. 2 shows the number of papers published between 2000 and 2010, in which either "superhydrophilic" or "superhydrophilicity" was used, according to ISI Web of Knowledge.

This paper reviews the last-decade of the research in this new field, and goes beyond it. It is organized as follows: first we review the definitions of hydrophilic solids and surfaces, including the most common misconceptions used, to show that there is a necessity for better quantification of this term. In the first section, we also provide examples of naturally occurring hydrophilic solids, which in recent years, are sometimes incorrectly called superhydrophilic. Then, we analyze the issue of complete water spreading on hydrophilic surfaces. High quality superhydrophilic surfaces cannot be fabricated without control over the hydrophilicity of materials used. For this reason we provide a brief overview of the methods commonly used for enhancing hydrophilicity of surfaces. Since all surfaces, particularly hydrophilic ones, are prone to contamination, this topic is also briefly reviewed.

In the second half of the paper, we define superhydrophilic surfaces and briefly discuss the means of enhancing spreading of a liquid over non-smooth surfaces. Because roughness and topography of the surface are critically important to the design of smart superhydrophilic surfaces and coatings, we critically review basic models that describe the behavior of liquid on rough surfaces. For all of the current advancements over the last few years, superhydrophilic coatings are still in their infancy but are just now moving toward several possible applications and commercialization. To appreciate this progress, in the last segment of this paper we review the research on superhydrophilic surfaces and coatings, as applied to different possible products and devices.

2. Defining hydrophilic surfaces and examples of hydrophilic materials

2.1. Solubility criterion

Historically substances, including molecules and ions, have been called *hydrophilic if they are readily soluble in water*, in contrast to hydrophobic substances that are poorly soluble in aqueous environments.[23] Hydrophilic solids are often *hygroscopic* and pick up water from the air.[24] Taking simple examples from the kitchen, both salt (sodium chloride; electrolyte) and sugar (sucrose; nonelectrolyte) easily dissolve in water, in large quantities, and both of these substances are therefore classified as hydrophilic, as per this general definition. Since surfaces of salt and sugar crystals are chemically identical to the bulk composition of their crystals, they must be hydrophilic as well. In fact, the mining and mineral processing community has recognized the hydrophilicity of natural salts such as halite (NaCl) and potash (KCl) for a long time. These minerals are not naturally floatable and air bubbles will not stick to their surfaces in water.[25] Their hydrophilicity has also been more quantitatively shown in new studies in which finite contact angles for saturated salt solutions were observed for some of the soluble salt crystals such as KI, KCl and $NaHCO_3$.[26,27] Other natural inorganic salts, the majority of organic pharmaceutics, and various artificial and natural organics including many polymers are known to dissolve enthusiastically in water as well. This means that we have already identified a large group of materials that are hydrophilic and have hydrophilic surfaces through simple solubility tests.

A dissolution test could be misleading however in identification of many solids having hydrophilic surfaces. The solubility process is governed by the balance of intermolecular forces between molecules of liquid and solid, together with an entropy change that accompanies the dissolution and solvation.[24] For example, detergents, although soluble in water, are classified under the group of *amphipathic* substances with dissolution in the aqueous phase controlled by their hydrophilic–lipophilic balance, the presence of type and the amount of polar functional groups.[28] Complete spreading of water drops placed on compressed discs of the detergents is prevented by a hydrophobic portion of the surfactant molecules.[29] In fact, alignment of surfactant molecules can produce either hydrophilic or hydrophobic moieties and crystallized surfactants form anisotropic crystals with planes of different wetting characteristics.[28] Arrangement and directionality of surface atoms and functional groups have, therefore, serious consequences in wettability of surfaces exposed to the wetting liquid. Further, strong covalent and ionic bonding in ceramics or metallic bonding in metals and alloys or large conformational entropy of long polymeric molecules prevents these solids from dissolving in water, though their surfaces usually have a higher affinity for water over air.

2.2. Polar spreads on polar

"*Like dissolves like*" is a widespread useful rule of thumb for predicting solubility of solids in water. This simplistic approach predicts that any solid with a similar chemical structure to water will dissolve in it; in other words, in water polar solids will dissolve. A similar concept has been adopted for surfaces so *hydrophilic surfaces are those having polarity, wherein surface molecules or their chemical groups have an electric dipole or multipole moment*. This leads us to the simple but still qualitative definition of hydrophilic surfaces: "*like spreads on like*" or "*polar spreads on polar*." What appears to be a rule of thumb cannot however predict hydrophilicity of metal surfaces. Metal surfaces, if not covered with an oxide layer, have nothing in common with the structure or polarity of water and yet water is known to spread out completely or nearly completely on noble metals such as gold, silver, copper and others (see the next section). In these systems, dispersion forces alone are adequate to induce water spreading on clean surfaces of noble metals.[30]

2.3. Fine particle partition

Finely divided solids with hydrophilic surfaces on which water spreads completely tend to sink in water when placed on its surface. Most often fine particles however are not so well wetted by water and they float on the water surface. The relative hydrophilicity/hydrophobicity of such fine particles can also be determined qualitatively by analyzing formation of Pickering emulsions,[31] in which powder particles tend to collect at the water/oil interface and act as stabilizers of an emulsion consisting of similar volumes of oil and water.[32] The interface becomes concave with respect to the liquid which better wets the particles;

i.e., an oil-in-water emulsion is formed with hydrophilic (90° > θ > 0°) particles and water-in-oil emulsion forms when particles are oleophilic (hydrophobic; θ > 90°).[33]

2.4. Contact angle value criterion

Contact with water or other polar liquid is preferred by hydrophilic surfaces over a nonpolar phase such as air or oil. It is therefore no surprise that a contact angle of 90° in a solid–water–air system has become the traditionally popular cut-off for designation of hydrophilic and hydrophobic surfaces. The distinction being that the surface is *hydrophobic* when the contact angle is larger than 90° and *hydrophilic* when the contact angle (θ) is <90°.[9] An exception to this ninety-degrees cut-off is seen in the mining and mineral processing community. Instead, *naturally hydrophobic minerals*, also called *naturally floatable minerals*, are those to which air bubbles attach in water, θ > 0°.[25,34]

A serious practical problem can emerge however when using the contact angle value in defining hydrophilic surfaces. It is related to the means with which the contact angle is measured. For example, solid state can dictate the measuring technique and measurements of contact angles on powder differ from that of the bulk specimen with a flat surface.[35] Further, the measured contact angle can be a different value depending on whether it is measured for water that advances (or recently advanced) over a dry surface of the solid or recedes (or recently retreated) from the wet solid surface.[36] The difference between *advancing contact angle* and *receding contact angle*, known as *contact angle hysteresis*,[37] is common to heterogeneous and rough surfaces,[38] and often depends on the volume of liquid used in measurements.[39] The contact angle hysteresis value also depends on whether the measurements are done under static or dynamic conditions and the rate of liquid movement.[40] Discussion of all the measuring techniques and obstacles with the measurements is beyond this review. Any discussion in this paper refers to static contact angles, including advancing and receding contact angles, measured on flat specimens rather than powder.

It is not always recognized that smooth and homogeneous surfaces can demonstrate the contact angle hysteresis.[41,42] Formation of stable thin water films of different thicknesses on hydrophilic surfaces is the reason behind this phenomenon. This was explained using the concept of disjoining pressure† introduced by Derjaguin in 1936,[43] which operates in a thin layer near the three-phase contact line. It was reported that on surfaces of quartz, glass, and metals,[43] two different water films, α-(adsorption) film and β-(wetting) film (both of different thickness), can coexist in equilibrium with the bulk water sitting on the solid surface.[41] α-Films are stable films and can be obtained in the course of the adsorption process, during, for example, contact angle measurements in air saturated with water vapors. β-Films, on the other hand, are metastable films and can only be obtained by decreasing the thickness of thicker films. As a consequence, the contact angle measuring technique and the methodology of deposition of liquid on a solid surface can influence the type of film that is formed on the hydrophilic surface and the surrounding vicinity of the liquid meniscus and, therefore, affect the measured contact angles.[44] We will ignore these problems in this sub-section and eventually return to some of them later.

As per our own practical experience, and many others, sessile-drop and captive-bubble techniques are often the methods of choice in static contact angle measurements for bulk materials with smooth surfaces. Contact angles are more reproducible if measured for the water drops/air bubbles having a base diameter of a few millimetres,[39] whose size is enlarged/reduced over the "dry" solid area before advancing contact angle measurements or reduced/enlarged over the "wet" solid area before receding contact angle measurements. In both cases, the shape of the water drop/air bubble must be stabilized, typically several seconds before contact angle reading.[44] The sessile-drop technique is most commonly used, outside mining and mineral processing laboratories, due to its simplicity. In the captive-bubble method, the required attachment of the gas bubble to the sample immersed in water or other liquid is not always possible if a thick water film remains stable on a solid surface. However, a benefit of the captive-bubble method is that both solid and gas phases are already saturated with water or water vapor and measurements of contact angle are carried out under more stable and reproducible conditions. Additionally, this technique more closely reflects flotation conditions of solid particles in processing of materials.[34]

Contact angles measured with either the sessile-drop or captive-bubble technique although often well reproducible should be repeated several times and statistically valid average values, together with a standard deviation, should be reported. Representative contact angle values can be used for not only identification but also for a classification of hydrophilic and hydrophobic surfaces. In fact, most of the contact angle values (advancing contact angles) published in the past were measured with these techniques, and the values are equal or close to what could be measured using the above-mentioned experimental protocol.‡

Now returning to our latest definition of the hydrophilic surface, defined by the water (advancing) contact angle less than 90°, it can be easily found that most natural and man-made materials could be grouped under this category, including biological membranes, the majority of inorganic minerals such as silicates, hydroxylated oxides, ionic crystals, metallic surfaces, and even the majority of polymers. In fact, it is easier to identify all hydrophobic materials and surfaces since hydrophilic ones are more abundant in nature. Only saturated hydrocarbon-based products such as wax, polyethylene, polypropylene, self-assembled monolayers with hydrocarbon functional groups as well as fluorine-based polymers, hydrocarbons, and monolayers are hydrophobic. Any inclusion of heteroatoms other than fluorine (particularly oxygen) into the structure of hydrocarbons, or even the presence of double or triple bonding, adds a polarity to the polymer or molecule reducing its hydrophobicity and introducing or enhancing hydrophilicity of the surface. There are

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† Disjoining pressure is defined as the difference in a thin liquid film adjacent to surfaces confining it and in the bulk of this liquid phase.

‡ In many publications published in recent years, if not in the majority, good protocols of contact angle measurements developed in the past are validated and issues like a minimum size of the drop necessary in measurements, multiple measurements, and sometimes the need for saturated environment are ignored. Also the contact angles are measured for just deposited small drops, without paying attention to advancing and receding contact angles and stabilization of the drop shape.

a number of minerals that are called naturally hydrophobic minerals including graphite, coal, sulfur, molybdenite, stibnite, pyrophyllites, and talc. However, the water contact angles on these minerals§ were reported to vary from 20 to 88°,[45] and therefore their surfaces do not fall under the above definition of hydrophobic. Further, there is not a known ceramic having a hydrophobic surface. Also water contact angles on metals and alloys are less than 90°. Metals (other than noble metals) and alloys, however, as a result of oxidation, are typically covered with a thin film of an oxide layer, often hydroxylated, and the contact angles measured on these materials represent wetting properties of this layer and not bare metal/alloy.

2.5. Recent definitions

van Oss recently proposed to use the free energy of hydration (ΔG_{sl}) as the absolute measure of hydrophilicity and hydrophobicity of both molecules and condensed phases.[46] Based on the analysis of the free energy of hydration for a number of different compounds, he found that hydrophobic compounds attract each other in water when $\Delta G_{sl} > -113$ mJ m^{-2}, whereas they repel each other when $\Delta G_{sl} < -113$ mJ m^{-2}.[46] He then used this (approximate) value as a cut-off between hydrophilic and hydrophobic materials.

Vogler[47] on the other hand proposed a cut-off between hydrophilic and hydrophobic surfaces based on the appearance of long-range attractive hydrophobic forces. Using experimentally measured hydrophobic forces, together with reported wetting characteristics of substrates used in force measurements, he concluded that hydrophilic surfaces are those with a water contact angle of $\theta < 65°$ and a water adhesion tension of $\tau > 30$ mN m^{-1}.[47] We will return to the models proposed by van Oss and Vogler in the next section.

2.6. Summary

Table 1 summarizes all definitions of hydrophilic surfaces discussed in this section, and lists major problems with these definitions. Since almost all of the solids, with the exception of several saturated and fluorinated hydrocarbons, have affinity to water beyond (always existing) London dispersion interactions, a large spectrum of hydrophilic surfaces surrounds our daily activities. Hydrophilic surfaces are not the same, however, and differences in wetting characteristics among them are expected. It would be important, therefore, to classify hydrophilic surfaces into sub-groups based on contact angle values, degree of hydrophilicity, strength of interactions with water, *etc.*

3. Measure of hydrophilicity and hydrophobicity

As for *hydrophilic surface* it is a surface that "*attracts water*" and the water contact angle should be less than 90°.[48] In many papers, as discussed earlier, a zero contact angle is expected for water on a hydrophilic surface. For example in the recent paper Sendner *et al.*[49] wrote: "*one experimentally easily accessible parameter characterizing the surface hydrophobicity is the contact angle which ranges from 180° (for a hypothetical substrate with the same water affinity as vapor) down to 0° for a hydrophilic surface*".

A true zero contact angle (in algebraic sense) has very serious implications for the energy balance expressed by Young's equation:[49,50]

$$\gamma_s - \gamma_{sl} = \gamma_l \cos\theta \tag{1}$$

where γ_s is the solid surface free energy, γ_l is the liquid surface free energy (the liquid surface tension), γ_{sl} is the solid/liquid interfacial free energy, and θ is the equilibrium contact angle.

Now, if the contact angle is equal to zero indeed, $\theta = 0$, then $\cos\theta = 1$ and eqn (1) reduces to:

$$\gamma_s - \gamma_{sl} = \gamma_l \tag{2}$$

This case occurs rarely, if ever, in practical systems and we will discuss this issue more extensively in the next section. The zero contact angle is the limit of applicability of Young's equation. Visually observed "zero contact angle" does not mean that eqn (2) applies to this situation. Such systems are better characterized by *the work of liquid spreading* W_s (also known as the spreading coefficient) *which is* defined as *the work performed to spread a liquid over a unit surface area of a clean and non-reactive solid (or another liquid) at constant temperature and pressure and in equilibrium with liquid vapor*:

$$W_s = \gamma_s - (\gamma_l + \gamma_{sl}) \tag{3}$$

In the case of two liquids, all components of eqn (3) are either liquid surface tension or liquid–liquid interfacial tension and are, therefore, measurable. In the case of solids, neither solid surface free energy nor solid–liquid interfacial free energy is easily measurable. However, if the liquid does not spread completely but forms a definite contact angle, then applying Young's equation allows the work of spreading to be easily calculated from measured contact angles and surface tension of liquid as long as $\theta > 0$:

$$W_s = \gamma_l(\cos\theta - 1) \tag{4}$$

It is difficult however to determine W_s for surfaces on which water spreads completely. Zero contact angle would imply zero work of spreading as well. However, $W_s > 0$ (no measurable contact angle) for a complete spreading and $W_s < 0$ for liquids that retreat to lenses with finite contact angle. Therefore the work of spreading could be used as a measure of a solid surface hydrophilicity. The concept is not entirely new as a similar approach was proposed by van Oss.[46]

van Oss proposed to use the free energy of hydration (ΔG_{sl}) as the absolute measure of hydrophilicity and hydrophobicity of both molecules and condensed phases.[46] The free energy of hydration (solvation) can be defined by means of the Dupre equation:

$$\Delta G_{sl} = \gamma_{sl} - \gamma_s - \gamma_l = -W_a \tag{5}$$

The absolute value of the free energy of hydration is equal to the work of adhesion (W_a). Instead of coping with immeasurable solid surface free energy and solid–liquid interfacial free energy,

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§ Static contact angles are often measured after attachment of an air bubble to the mineral immersed in water.

Table 1 Definitions of hydrophilic surfaces, along with their major problems, reviewed in this paper

No.	Definition of hydrophilic surface	Problem
1.	Readily soluble in water	Metal oxides, ceramics and amphipathic substances do not dissolve in water, although some of them are hydrophilic
2.	Like spreads on like (polar spreads on polar)	Metals do not fit into this category
3.	Partition of particles between the oil and aqueous phase and formation of either water-in-oil or oil-in-water emulsions	Most of the particles sit at the water–oil interface and quantification of their hydrophilicity is not possible
4.	Contact angle less than 90°	Vast majority of solids, although their bare surface characteristics are very different
5.	Thick water film remains stable: no gas bubble attachment ("zero" receding contact angle)	Often caused by β film (metastability). What is the advancing contact angle?
6.	Free energy of hydration less than -113 mJ m^{-2}	Scale built based on research with compounds instead of solids and more research is needed to determine the value for solids. Solids are often anisotropic—orientation and packing of molecules and atoms will contribute to hydration energy
7.	No long-range hydrophobic forces	Hydrophobic forces between surfaces still stir controversy regarding their origins, range of operation, and wetting characteristic of surfaces between which they operate

van Oss *et al.*[51–53] proposed to split the surface free energy into components representing Lifshitz–van der Waals and acid–base interactions. Components of the solid surface free energy or liquid surface tension are determined from contact angle measurements using at least three different probing liquids of varying surface tension and polarity. This model however is beyond the scope of this review and will not be discussed here.

van Oss also analyzed the free energy of hydration for a number of different molecules and found that hydrophobic molecules which attract each other in water have $\Delta G_{\mathrm{sl}} > -113$ mJ m^{-2}, whereas for hydrophilic molecules $\Delta G_{\mathrm{sl}} < -113$ mJ m^{-2}.[46] He then used this (approximate) value as the inversion point between hydrophilic and hydrophobic materials.

Eqn (5) can be further modified by substituting Young's equation:

$$\Delta G_{\mathrm{sl}} = -\gamma_{\mathrm{l}}(\cos\theta + 1) \qquad (6)$$

Considering the crossover value between hydrophilic and hydrophobic surfaces proposed by van Oss, we can calculate the value of the equilibrium contact angle from eqn (6) which describes the transition between hydrophilic and hydrophobic surfaces. The value is $\theta \approx 56°$ for $\Delta G_{\mathrm{sl}} = -113$ mJ m^{-2}, and as the result indicates a zero water contact angle is not needed for the solid surface to be called hydrophilic. Additionally, this value suggests that hydrophobic surfaces are already those with $56° < \theta < 90°$. It is interesting to note that a similar cut-off between hydrophilic and hydrophobic surfaces was suggested by Vogler in 1998.[47] Based on the analysis of experimental long-range attractive (hydrophobic) forces he came to the conclusion that hydrophilic surfaces are those with a water contact angle of $\theta < 65°$ and a water adhesion tension of $\tau > 30$ mN m^{-1}. The adhesion tension is defined as:

$$\tau = \gamma_{\mathrm{l}}\cos\theta \qquad (7)$$

Taking into account previous recommendations, we propose the classification of hydrophilic and hydrophobic surfaces based on the contact angle, work of spreading, free energy of hydration and water adhesion tension as shown in Table 2. Hydrophilic surfaces are those on which water spreads completely, visually "zero contact angle." The vast majority of materials, called here weakly hydrophilic and weakly hydrophobic, are those on which water films are unstable and water beads (lenses form) with a contact angle less than 90°. Hydrophobic surfaces are those commonly recognized with water contact angles at least 90°. We also include superhydrophilic and superhydrophobic surfaces in Table 2 but they will be discussed later.

Table 2 Proposed measures of hydrophilicity and hydrophobicity of solid surfaces

	Measure of hydrophilicity/hydrophobicity (20 °C)			
Type of surfaces	Contact angle/°	Water adhesion tension/mJ m^{-2}	Work of spreading/mJ m^{-2}	Energy of hydration/mJ m^{-2}
Superhydrophilic (rough with $r > 1$)	$\sim 0^{a}$	$\geq 73^{b}$	$\geq 0^{b}$	$\leq -146^{b}$
Hydrophilic	~ 0	≥ 73	≥ 0	≤ -146
Weakly hydrophilic	$(56\text{–}65°) > \theta > 0$	$73 > \tau > (30\text{–}40)$	$0 > W_{\mathrm{s}} > -(32\text{–}42)$	$-113 > \Delta G_{\mathrm{sl}} > -146$
Weakly hydrophobic	$90° > \theta > (56\text{–}65°)$	$(30\text{–}40) > \tau > 0$	$-(32\text{–}42) > W_{\mathrm{s}} > -73$	$-73 > \Delta G_{\mathrm{sl}} > -113$
Hydrophobic	$120° > \theta \geq 90°$	$0 \geq \tau > -36$	$-73 > W_{\mathrm{s}} > -109$	$-36 > \Delta G_{\mathrm{sl}} > -73$
Superhydrophobic (rough with $r > 1$)	$\theta > 150°^{a}$	$\tau \leq -63^{b}$	$W_{\mathrm{s}} \leq -136^{b}$	$\Delta G_{\mathrm{sl}} \geq -10^{b}$

[a] Apparent contact angle. [b] Estimated based on apparent contact angles and using eqn (4), (6), and (7).

Table 3 Solids on which complete water spreading was observed. References are provided in the text

Type of solids	Examples of solids on which water spreads
Minerals	Cleaved mica, native gold and silver, quartz, trona, halite
Metals	Gold, copper, silver, chromium
Ceramics	Silica, TiO_2 and other oxides with dense population of OH groups, glass
Salts	NaCl, NaF, Na_2CO_3
Biological specimens	Biological membranes and lipid layers

Only if these solids are freshly prepared and/or their surfaces are carefully cleaned.

Now the question which we address in the next section is: can water spread completely on flat hydrophilic materials?

4. The case of complete spreading on a flat surface

As per discussion in the previous section, the first group of hydrophilic solids that we identified is the group of soluble salts. Are these solids perfectly wetted by water? This question has only partially been answered in the technical literature. Past research clearly showed that air bubbles do not attach to either soluble or semi-soluble minerals in water (saturated with these solids).[25] This suggests that water films remain stable on surfaces of these minerals. Whether water will spread out on dried surfaces of these minerals is not so obvious, however. For water-soluble solids such as salt or sugar, the measurements of advancing contact angles are either impossible or experimentally difficult and have results which are challenging to interpret. The advancing water contact angle for such "reactive solids"[54,55] cannot be determined and the angles measured represent values for water with dissolved solid, measured for either partial saturation (under non-equilibrium conditions) or saturated aqueous solutions with surface tensions that differ from the surface tension of pure water.[26,27] The substance dissolution also changes the surface topography of the solid, adding a roughness component to the complexity of the three phase system examined. However, infinite advancing water contact angle values have been measured. For example, Miller *et al.*[26,27] determined contact angles on a number of soluble salt crystals. Saturated solutions spread completely on NaCl, NaF, and Na_2CO_3 whereas contact angles as high as 8, 20 and 25° were reported for KCl, $NaHCO_3$, and KI, respectively.

Further, commonly used pharmaceutical products are made of a hydrophilic drug powder coated with a protective layer to reduce the kinetics of drug dissolution. Although the drug without protective coating dissolves in water, drops placed on compressed discs (or on single crystals if available) of these anisotropic organic solids will typically not spread out completely. Water contact angles on insulin and lactose as high as 36–42° and 22–28°, respectively (E. Chibowski and J. Drelich, unpublished), were estimated in our research using a thin layer wicking technique;[56,57] these angles are probably far from equilibrium since neither powder nor water could be equilibrated in such tests.

It was reported in the literature that water can spread out completely or nearly completely on just a few nonporous and smooth materials (Table 3). These include glass,[1] gold,[58] copper,[59] silver,[59] chromium,[24] selected oxides (having OH groups on the surface)[60,61] including quartz[62] and amorphous silica surface,[63] biological specimens (such as biological membranes and lipid layers),[46] and cleaved mica.[64] However, this was only observed if these materials were freshly prepared and/or their surfaces were carefully cleaned.[1,65,66] The surfaces of these solids have strong affinity towards water molecules and have been commonly recognized as hydrophilic, sometimes called solids with strongly hydrophilic surfaces to differentiate them from other hydrophilic surfaces on which the water contact angle is larger than 5–10° (but less than 90°).¶

At first glance, zero contact angles should be fairly common. According to Young's equation, when $\theta = 0$: $\gamma_s \geq \gamma_l + \gamma_{sl}$.‖ If the water–solid interfacial free energy approaches a near zero value, which probably is the case for solids capable of interacting with water molecules through hydrogen bonding such as oxides with hydroxyl groups on the surface, then all solids with $\gamma_s \geq 72.8$ mJ m^{-2} at ~22 °C could satisfy the conditions of perfect water spreading on them. In fact, metals, alloys, ceramics, and ionic salts[67] all have *surface free energy* higher than 72.8 mJ m^{-2} and the only known materials with surface free energies less than that of water are organic polymers.[68]

This raises the question if such a wide variety of high-surface energy materials are available to us, why is water spreading and development of thick films not commonly observed on them? Why don't these materials retain an adsorbed water film at all times? The formation of water films on many inorganic materials, including natural minerals, could probably be observed if oxygen and volatile organics are eliminated from the material's environment. The high energy of material surfaces is a short-lived state because constituents of surrounding phases either chemically react with the material or adsorb on its surface or both in an attempt to reduce the tensions on the surface and produce a more stable system. An example is an oxide layer, which covers the majority of metals as well as many other single-elemental materials and ceramics. It is the result of chemical reaction of surface elements with oxygen from air or aqueous phases during either material production or service. Mercaptans and many other organic compounds that humans, and other living species, breathe out, diffuse and adsorb, often through strong chemical bonding, on solid surfaces. Any changes to a material's surface reduce its surface tension, changing also the surface affinity towards water. We will return to the issue of surface contamination in a separate section, whereas corrosion of materials is ignored in this paper and we only discuss the surfaces that remain stable during the time of examination of wetting properties resulting solely from physical interactions.

Is this possible however to attain zero value for the *apparent* (water) *contact angles*** on smooth, homogeneous and inert surfaces of the above hydrophilic materials? The question is not easy to answer as determination of the contact angles less than 5–10° with commercial contact angle measuring instruments, which

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¶ It is also quite common to divide surfaces for hydrophilic ($\theta_W < 5$–10°) and partially hydrophilic (~10° < θ_W < 90°).

‖ It should be recognized that the Young's equation does not apply to the cases of zero apparent contact angle.

** Apparent contact angle also known as *macroscopic contact angle* (sometimes also called *geometric contact angle*) is that observed with the optical means on any type of surface: smooth, rough, and/or heterogeneous.

typically rely on an image analysis of the shape of either liquid drop or meniscus, is rather difficult.

Since most scientific research requires that measurements of contact angles are conducted on clean surfaces, we concentrate our attention on such systems. But even if the surface of hydrophilic minerals, metals, or ceramics is well prepared, measurement of a macroscopic water contact angle of zero value is rare, if measured accurately at all, as discussed earlier. It is usually the contact angle that is near zero value. Why a zero water contact angle is difficult to observe on smooth surfaces of hydrophilic materials has been partially answered by Russian scientists through the concept of disjoining pressure and formation of stable thin water films, in fact with *microscopic contact angle*†† that differs from *macroscopic contact angle*.[69–73] Autophobic properties of a thin film often prevent formation of thick water films. Qualitatively, this can be explained by changes in the surface free energy of a solid surface modified by a water film and properties of the water film that differ from the bulk water. Strong hydrophilic surfaces affect diffusion, rotation, and orientation of water molecules located near the hydrophilic solid surface. As a result, the interfacial water molecules, usually from one to three layers of molecules, are more organized than in the bulk.[69–73] Also an interface, and therefore tension, is expected between the ordered thin film of water and the amorphous water bulk.[74] The tension at the surface of an organized water layer, if this could be measured, should be less than the surface tension of water.[75] Indeed, several measurements showed finite contact angles for water placed on ice, ice representing the frozen structure of water.[75–77] For example, Knight reported a (receding) contact angle of 12° for water on a somewhat rough surface of ice at a temperature below 0 °C.[76] At a similar temperature, Ketcham and Hobbs found a water contact angle of about 20°.[77] More recently, the surface free energy of ice was estimated through contact angle measurements with different liquids by van Oss *et al.*[75] and found to be 69.2 mJ m^{-2} as compared to 75.8 mJ m^{-2} for water at 0 °C. This low value of the surface free energy of ice explains the relatively large water contact angles measured experimentally.

The presence of molecular or nanometre-sized thin water films on hydrophilic materials is probably more widespread than commonly recognized. Although the measurements of disjoining pressure of water films are still not popular, stable thin water films, including adsorption α-films and wetting β-films, were recorded on a few hydrophilic surfaces of materials such as quartz, glass, and metals.[43] α-Films are stable films and can be obtained in the course of the adsorption process, during, for example, contact angle measurements in air saturated with water vapor. β-Films, on the other hand, are metastable films and can only be obtained by decreasing the thickness of thicker films. It cannot result from water spreading.

In summary, the existence of true zero contact angles is still a question worth further study. In practice many researchers use 5 or 10° as an arbitrary cut-off for complete spreading of water on hydrophilic surfaces, as well as superhydrophilic surfaces discussed later.

5. Common methods to produce hydrophilic surfaces

The enhancement of hydrophilicity of surfaces can be approached through either deposition of a molecular or microscopic film of a new material, more hydrophilic than the substrate, or by modification of the chemistry of the substrate surface. Molecular modification or deposition of coatings is more common for inorganic substrates whereas modification of surface chemistry is broadly used in the case of polymeric materials. In this section, the most commonly used methods for making surfaces hydrophilic are briefly reviewed. Examples of applications for fabrication of superhydrophilic coatings will be discussed later.

5.1. Deposited molecular structures

A number of organic molecules adsorb from either solution or a vapor phase on selected solids, spontaneously organizing into self-assembled monolayers, changing wetting characteristics of the substrate.[78] The most commonly studied densely packed molecular structures include alkanethiols on gold,[79,80] silver,[81–83] copper,[81–83] platinum,[84,85] and palladium,[86] chlorosilanes on silicon oxide,[87–90] aluminium,[91,92] titanium[93] and other oxides,[93] phosphonic acids on titanium,[94,95] aluminium,[96,97] and other oxides.[95] Both mono- and multi-layers can be deposited mechanically through a Langmuir–Blodgett film technique, although physically deposited multilayers suffer from poor stability when contacted by liquids.[78] Deposited organic layers make the surface hydrophilic if the end group is polar, and not a saturated hydrocarbon-based group or fluorinated group. The groups with the highest hydrophilicity are probably those capable of interacting with water molecules through hydrogen bonding such as –OH, –COOH and POOH.[79,80,98] On none of these layers, however, has a zero water contact angle ever been recorded.

Beside arranging self-assembled monolayers of chemically bonded short functional molecules on inorganic surfaces, a great deal of research has focused on coating of materials with macromolecules and biomacromolecules, which is especially popular in modification of polymers contacting biofluids, including blood.[99] Albumin[100–102] and heparin[103–105] have been widely used as biomacromolecules. Among synthetic polymers, poly(ethylene glycol)[99,106,107] and phospholipid-like[107–111] macromolecules have been studied extensively. In the typical bioengineering applications of such coatings, however, the hydrophilicity of grafted or physically adsorbed dense structures of biomacromolecules or synthetic macromolecules is usually of secondary importance and both biocompatibility and fouling resistance are more important. These protective coatings are intended to prevent protein adsorption when materials come into contact with biological fluids.[112]

5.2. Modification of surface chemistry

Over the last few decades, many advances have been made in developing surface treatments by plasma, corona, flame, photons, electrons, ions, X-rays, γ-rays, and ozone to alter the chemistry of polymer surfaces without affecting their bulk properties.[113,114] Plasma treatment, in air or oxygen environment,[115,116] corona[117,118] and flame[117,119] treatments are the most distinguished techniques in oxidation of polymer surfaces.[120] In

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†† Microscopic contact angle is that observed at a junction of the three phases at a scale of several micrometres or smaller.

both plasma and corona treatments, the accelerated electrons bombard the polymer with energies 2–3 times that necessary to break the molecular bonds, producing free radicals which generate cross-linking and react with surrounding oxygen to produce oxygen-based functionalities.[115] Polar groups being typically created on the surface are hydroxyl, peroxy, carbonyl, carbonate, ether, ester, and carboxylic acid groups.[118] In flame treatment, surface combustion of the polymer takes place with formation of hydroperoxide and hydroxyl radicals.[119,121] Oxidation depth through flame treatment is around 5–10 nm, and over 10 nm for air plasma treatment.[122] Plasma, corona and flame treatments end in extensive surface oxidation and result in highly wettable surfaces. Polar groups produced during surface oxidation have a tendency to be buried away in the bulk when in contact with air for extended period of time, but they remain on the surface when in contact with water or any other polar environment.[123]

Polymers also oxidize and degrade under a UV (ultraviolet) light, and, for example, polymeric outdoor consumer products need addition of UV absorbers when exposed to the sunlight to inhibit discoloration, cracking, and fading.[124,125] UV light has a wavelength in the range 10 nm to 400 nm (energy of 3 eV to 124 eV), the incident photons of which have enough energy for breaking intermolecular bonds of most of the polymers, promoting structural and chemical changes of the macromolecules.[126] The exposure of the polymer to UV radiation causes chain scission, crosslinking, and increases the density of oxygen-based polar groups at the substrate surface, making the surface more hydrophilic.[127–130] Recently, UV light has been used to control polymerization reaction and pattern microstructures of different wettability for a variety of applications of microfluidic devices.[131]

Alkali treatment of polymers, especially at elevated temperature, can also enhance surface hydrophilicity of polymers.[132–134] Hydroxyl and carboxyl groups are among the hydrophilic groups formed on the surface of polymers such as polyolefins and polyethylene terephthalate during their etching with concentrated bases.[135,136]

Finally, anodic potential was used to electrochemically treat a conductive oxide surface and control its wetting characteristics.[137,138]

6. Contamination of hydrophilic surfaces and their cleaning

The hydrophilic surface must be kept free of contaminants such as airborne organics, moisture and dust particles to preserve its wetting characteristics. A freshly prepared hydrophilic surface when exposed to the laboratory environment tends to achieve its lowest energy (most stable state) by instantaneous changes at the surface, *e.g.*, adsorption of water molecules or organic contaminants. In this way, contamination of hydrophilic surface and consequently a reduction of surface energy occur naturally for many materials.

The problem of contamination of high-energy surfaces with organics is not always well recognized in many laboratories. For example, there had been a long standing controversy in both the mining and mineral processing and surface chemistry communities about the hydrophobicity of metals such as native gold and silver.[139,140] Water contact angles as high as 55–85° were reported in the literature for gold surfaces.[140,141] After the work of Bewig and Zisman[142] and then of Schrader,[59,143] as well as others,[58,140] it became clear that pure water can spread out completely over the surface of a freshly prepared clean metal such as gold,[58,140,142,143] platinum,[142] copper,[59] and silver.[59] Physical interactions at the metal–water interface are strong and consist solely of dispersion forces.[30] The Hamaker constant for metals is an order of magnitude higher than the Hamaker constant for water.[24] Unfortunately, reports on stability of hydrophilic surfaces in the laboratory environment as well as typical organics attracted by hydrophilic surfaces and kinetics of their adsorption are rare. Among those, Bewig and Zisman[144] showed that even nonpolar vapors of hexane and benzene adsorb on clean surfaces of metals and the temperature of a contaminated metal must be raised by at least 100° to remove the last monolayer of these hydrocarbons.

One of the first systematic studies reported on the phenomenon of contaminant adsorption at high-energy surfaces was presented by Bartell and Bristol in 1940,[145] although the protocols and precautions to prevent contamination of specimens in contact angle measurements were not recognized until decades earlier (see, for example, a brief review in the book by Sutherland and Wark[34]). Bartell and Bristol showed that the wetting characteristics of quartz and glass depend not only on the state of the solid surface but also on the particular day of contact angle measurements. They also found that the measured water contact angles were closely related to the degree of humidity in the atmosphere. White[146] reported the kinetics of contact angle change for water drops placed at the surfaces of mica and oxidized surfaces of nickel, aluminium, and nichrome when these materials were exposed to laboratory air. He observed a fast increase in contact angle values in the first 10–20 hours and only a few degrees after that in the next two days. The water contact angle increased from nearly zero value to 15–20° for mica and nickel and to 32–37° for aluminium and nichrome.

White[146] also showed that the vapor of mineral oil adsorbs less on glass and mica than aluminium and magnesium with transition metals showing the most. Similar observations were made earlier for the adsorption of fatty acids from solutions and vapor phase which showed that there is less adsorption on mica, gold, platinum and chromium than on nickel, iron and copper.[147] Both studies revealed that surfaces become contaminated at different rates and to different levels, as a result of adsorption driven by molecule–surface interactions. White also proposed that organics can be gathered from the air by adsorption onto oxidized metal surfaces and therefore used as filling media in storage compartments to maintain surface cleanness of lower energy specimens such as glass or mica.

Even small quantities of organic contaminants make a large difference in wettability of hydrophilic surfaces.[34,58,140] A typical experiment relies on storage of a sample in laboratory air and monitoring periodically the changes in contact angles. Since air quality in each lab is ill-defined and composition can vary substantially from lab to lab,[148] the results can be poorly reproducible. They are however very useful in revealing the problem of airborne contamination that researchers can deal with in regular laboratory activities.

Recent studies suggest that a change of tens of degrees in water contact angles can be observed on glasses and metal oxides as a result of surface contamination with airborne hydrocarbons.[65,66,149] When cleaned, metal oxides[65,149] and commercial glasses[66] demonstrate a water contact angle at a level of a few degrees. Strong hydrophilicity of these materials was reported to degrade, however, during storage in laboratory air under ambient conditions. In 3 to 4 days of storage, the water contact angle increased to 50–60° for aluminium oxide[149] and tin oxide,[65] 35–38° for silica, 80–90° for titanium oxide and chromium oxide, and to above 100° for zirconium oxide.[65] The water contact angle increases from 20 to over 50° for glasses exposed to ambient air for the same time.[66] Interestingly, in the case of both glasses and metal oxides, Takeda *et al.*[65,66] found that the surface OH groups attract organic contaminants and OH group density correlates with the adsorption of organics from the atmosphere.

Hydrophilic surfaces adsorb water from the laboratory environment and the amount of water sitting on the hydrophilic surface depends on the relative humidity. Although the phenomenon of formation and stability of water films at hydrophilic surfaces is important in many areas of science and technology, such as mineral processing, the electronic industry, microtechnology, and many others, not enough research has been done to study the properties of adsorbed water films, including monolayers. It is generally accepted that under ordinary atmospheric conditions, hydrophilic surfaces adsorb at least a monolayer of water. For example, a clean glass surface is covered with a monolayer of adsorbed water at relative humidities of around 30–50% at 20 °C.[150] Formation of a water film composed of as many as twenty molecular layers, or more, may occur at the clean surface of high-energy solids, especially at high relative humidities, >90–95%.[151] For example, Rhykerd *et al.*[152] measured ellipsometrically the thickness of the adsorbed water film on a fused silica surface and found it ranging from 2.4 to 9.0 nm, depending on the water vapor pressure. Staszczuk[153] used gas chromatography to determine the water adsorption isotherm on quartz at 20 °C and found that about 16 statistical water layers adsorbed from a gas phase saturated with water vapor. Also, similar experiments using the chromatographic technique showed that about 15 statistical water layers may adsorb onto a marble surface.[154] Water films with thicknesses from 1.0 to 8.0 nm were also reported for muscovite mica.[155]

Water if already present on the hydrophilic surface can probably prevent or at least slow down the adsorption of organic contaminants. Unfortunately the water surface also attracts organics, surface-active contaminants, when open to the laboratory air. Volatile organics are in exhaled breath[156] and, therefore, always contaminate laboratory air. After adsorption on a layer of water at sufficient quantities, it is possible that they destabilize the water film, exposing the solid surface to them; something that was probably never studied in detail. Good practice in many surface chemistry labs is, therefore, to keep clean hydrophilic samples immersed in water before using them for experimentation and testing. Such storage is obviously acceptable if the sample's integrity and surface chemistry remain intact in water.

Many experimental contact angles are unreliable because of the failure to work with clean solid surfaces. There should be no justification for work with surfaces that have not been prevented from systematic and accidental contamination, and properly tested for contamination. All instrumentation used in preparation of specimens (cutting, polishing, sputtering) should be freed from grease and any other organics, *e.g.* by washing it with appropriate (nonionic) detergent solutions, organic solvents (benzene, ethanol, chloroform), and/or acids (sulfuric acid–dichromate mixture). Annealing of samples at high temperatures, >500 °C,[146] oxidizes organics to carbon dioxide and water, this approach can significantly alter the chemistry of the surface and, therefore, is only acceptable to certain inorganic materials. Surfaces of oxides such as quartz, for example, undergo dehydration at such high temperatures which results in the increase of a nearly zero water contact angle to 30–40°.[62,157] Thus, the oxide surfaces are not necessarily well wettable by water when clean, and the water contact angle is closely related to the density of OH groups on the oxide surfaces.[62,157] Oxide surfaces can be cleaned by degreasing and boiling in 30% hydrogen peroxide.[146] Specimens should be always handled with latex gloves and never kept close to the mouth as breath contains tens, if not hundreds, of volatile organics.[156]

The majority of surface treatments that are commonly used for modification of surface chemistry of polymers such as plasma, corona, flame, photons, electrons, ions, X-rays, γ-rays, and ozone treatments, briefly reviewed in the previous section are also effectively used in cleaning substrates. The use of a particular technique is rather dictated by its availability and applicability to a particular type of solid.

7. Defining superhydrophilic (superwetting) surfaces

In our previous paper,[158] we proposed a definition for superhydrophilic (superwetting) surfaces. We also briefly discussed meanings to facilitate superhydrophilicity. Here we repeat our definition and then discuss issues related to manipulation of such surfaces through the control of surface roughness. Before doing that however, we start with a definition of the superhydrophobic surface since the term "*superhydrophobic surface*" appeared in the literature prior to the term "*superhydrophilic surface*". Both terms are opposite to each other with respect to solid surface wetting properties. In the last few years, superhydrophobic materials and coatings have attracted attention from a large number of research laboratories, all over the world, as evidenced by the explosion of published papers (see several reviews[1–15] on this topic and references therein). The term superhydrophobicity was introduced in 1996 by Onda *et al.*[16,17] to describe unusually high water contact angles, not observed on flat and smooth hydrophobic materials. The commonly accepted meaning of superhydrophobic surface is a surface on which the water (advancing) contact angle is at least 150°, and the contact angle hysteresis as well as the sliding (or rolling off) angle‡‡ do not exceed 5–10°. Superhydrophobic surfaces were inspired by biological specimens,[159–178] and their artificial substitutes were manufactured by chemical, physical and/or mechanical modifications of both organic and inorganic materials.[1–15] A common feature (not always necessary) of superhydrophobic surfaces is their proper two-level topography, with micro- and nano-sized asperities/posts, similar to what was first observed on lotus leaves

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‡‡ Sliding/rolling angle is the minimum angle of sloped solid at which water (liquid) drop rolls off the surface.

and 200 other water-repellent plant species.[159–177] Because the scope of this article is focused on superhydrophilic (superwetting) surfaces, the superhydrophobic ones will not be described in detail.

Since surface roughness is a necessary feature of superhydrophobicity and superhydrophilicity, it can be said that the principle of these phenomena was actually found several decades ago by Wenzel[179] and Cassie and Baxter[180] who described contact angles and different mechanisms of wetting on rough surfaces. The validity of their equations in description of liquid wetting at superhydrophobic or superhydrophilic surfaces will be discussed later.

As mentioned above, the opposite to superhydrophobic is superhydrophilic surface. This type of surface is also of a great interest now,[138,181–207] although a strict definition of superhydrophilicity remains to be seen.[13] The superhydrophilic surfaces may have many practical applications like antifogging, antifouling or self-cleaning, and others.[138,208–215] Superwetting is also important in biological systems, like cell activity, proliferation, signaling activity, *etc.*[216] It is generally accepted that the first prerequisite for a surface to be superhydrophilic (superwetting) is that the water (liquid) apparent contact angle is less than 5°. In our previously published note[158] we suggested to refer to surfaces as being *superhydrophilic (or superwetting) surface only for a textured and/or structured surface (rough and/or porous) possessing roughness factor (r = ratio of real surface area to projected surface area) defined by Wenzel equation*[179] *larger than* $r > 1$, *on which water (liquid) spreads completely*. In the light of the above, clean glass or freshly cleaved mica surfaces (as well as other examples of hydrophilic surfaces discussed earlier) are not superhydrophilic ones, although water can spread over them completely. Such surfaces are simply naturally hydrophilic. In other words, superhydrophilic (superwetting) surfaces cannot be achieved without manipulation of the roughness of hydrophilic materials.

In terms of a wicking parameter, W_s:

$$W_s = \gamma_{sv} - \gamma_{sl} = \gamma_l \cos\theta > 0 \tag{8}$$

A minimum roughness of the surface necessary to initiate liquid wicking that results in zero apparent contact angle is commonly predictable through the Wenzel equation (discussed in the next section):

$$r \geq \frac{1}{\cos\theta} \tag{9}$$

Fig. 3 shows the correlation between the contact angle on a smooth surface of the material (Young's contact angle; θ) and the minimum value of the roughness factor (r) that is necessary for the rough surface of this material to promote complete spreading of the liquid. It shows that with a moderate roughening of the substrate surface, $r = 1.2$–2, superhydrophilicity or in general, superwetting, should be possible on any material having an intrinsic contact angle less than 60°. For materials with $\theta > 65$–$70°$, the roughening might not be a practical approach due to the extremely high values needed for r, although theoretically liquid on any rough material should spread to zero (or nearly zero) apparent contact angle. In practice however, it is also observed that liquid penetration into the rough structure of the substrate might be difficult. For example, the results presented by Onda *et al.*[16,17] revealed the limitation of liquids to spread completely on extremely rough substrates.

Liquid drops can remain suspended on many rough and textured surfaces even if the condition given by eqn (9) is fulfilled. It relates to the three-phase system trapped in a meta-stable state,[217] and such surfaces should be treated more like porous or solid–air composite materials.[218,219] The invasion of the liquid can be inhibited on materials of particular design, geometry, size and contour of surface features and protrusions, and an energetic barrier associated with unfavorable geometry of the substrate for liquid wicking must be overcome.[9,220–224] This energetic barrier if larger than the available thermal energy[7] needs to be overcome by mechanical means such as vibrations,[225,226] impact,[227,228] or load imposed on the drop.[224,229] By manipulating liquid re-entrant profiles on rough features, opposite effects are often desired in which the lack of liquid penetration into protrusions of the rough and textured surface, with liquid drops remaining suspended, is beneficial for the design of superhydrophobic and superoleophilic surfaces.[230,231]In fact special designs are not necessary and using structures of nanotubes[232] and nanofibers[8,233] as a coating can often provide similar results.

8. Surface topography effects on wetting: common models and their limitations (Wenzel and Cassie–Baxter models)

It is now well accepted that surface topography plays a crucial role in liquid spreading on a solid surface. The surface topography may either enhance or reduce wetting, depending on the contours and size of the protrusions. There are two possible cases of solid surface wetting that may occur, which were outlined a long time ago by Wenzel[179] and Cassie–Baxter.[180] If the liquid fills in the 'valleys' of the rough surface then the apparent (observed) contact angle θ_{rough} is described by Wenzel's equation:

$$\cos\theta_{\text{rough}} = r\cos\theta \tag{10}$$

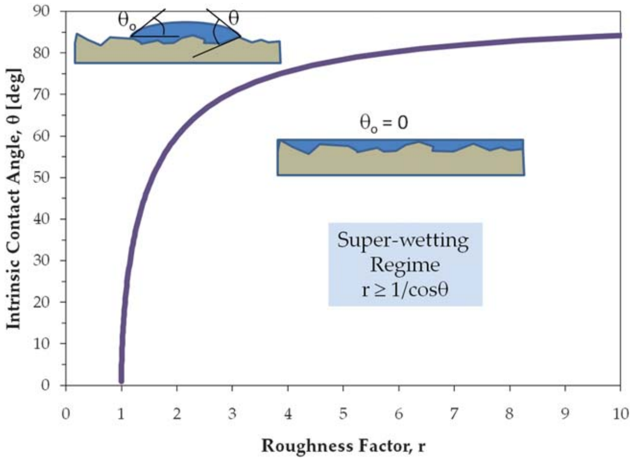

Fig. 3 Minimum values of roughness factor necessary to promote complete spreading of liquid on a surface with varying Young's (intrinsic) contact angle.

where r is the roughness parameter, which expresses the ratio of the true solid surface area to its horizontal projection, and is larger than 1, and θ is the equilibrium contact angle that would be measured on a flat surface of the same solid. It can be said that 'chemistry' of the surface is reflected in θ while the effect of the roughness involves the r parameter.[234] McHale *et al.*[234] stated that Wenzel's equation also predicts changes in the apparent contact angle θ_{rough} caused by changes in the equilibrium contact angle $\Delta\theta$ induced by surface chemistry, which is given as follows:

$$\Delta\theta_{\text{rough}} = r\left[\frac{\sin\theta}{\sin\theta_{\text{rough}}}\right]\Delta\theta \tag{11}$$

They concluded that the change in surface chemistry "*is amplified by the rough surface into a large change in the observed contact angle*". According to eqn (11) for $\theta = 90°$ the amplification factor is equal exactly to the roughness factor r in eqn (10) and approximately for the angles around 90°.[234]

Wenzel's equation (eqn (10)) indicates that for suitably large roughness the apparent contact angle drops to zero degrees, $\theta_{\text{rough}} = 0$, or increases up to 180°, $\theta = 180°$ ("roll-up of the liquid"). The boundary between these two cases is determined by $\cos\theta = \pm 1/r$,[234] see eqn (9).

In the case of narrow valleys between surface protrusions it may happen that liquid penetration is inhibited with the liquid remaining on top of the protrusions. As a result, the air is trapped beneath the liquid and the liquid then sits on what is commonly referred to as a composite surface; *i.e.*, on asperities of the solid separated by air gaps. In such a case the liquid contact with the solid surface is greatly reduced and the system is described by the Cassie–Baxter equation:[180]

$$\cos\theta_{\text{C–B}} = \varphi_s \cos\theta - (1 - \varphi_s) \tag{12}$$

where φ_s is the fraction of the liquid base in contact with the solid surface, $\varphi_s < 1$, and $(1 - \varphi_s)$ is the fraction of the liquid base in contact with air pockets. Air is not wetted by water and therefore the water/air contact angle equals to 180°. Hence this cosine term leads to the minus sign in the second term of eqn (12). A complete roll-up of a droplet cannot take place on a flat solid surface since there is no natural or man-made hydrophobic material with a water contact angle larger than 118–120° (only fluorinated materials/surfaces such as PTFE can exhibit such hydrophobicity). Nevertheless, the Cassie–Baxter equation (eqn (12)) predicts that an enhancement of the contact angle up to its superhydrophobic value (>150°) can be obtained by roughening of the solid surface and by manipulating its topography.

Both the Wenzel and Cassie–Baxter equations suggest that increasing the surface roughness (or texturing) leads to superhydrophobic states, and by changing the surface chemistry and making the solid more hydrophobic we can observe a transition from the Wenzel to the Cassie–Baxter state.[234] Metastability of the liquid configuration is the common problem for liquid in contact with rough and/or textured surfaces, promoting the Cassie–Baxter state. Extra mechanical energy through, for example, vibration or pressure loads on the liquid is sometimes necessary to reinforce a change from a metastable to a stable state. The Cassie–Baxter state is usually easy to recognize as liquid droplet will roll-off the rough surface at a low tilting angle. In the case of the Wenzel state, the droplet sticks to the surface and a large tilting angle is required for roll. It should be noted that a low tilting angle corresponds to a low contact angle hysteresis, *i.e.* the difference between advancing and receding contact angles.

However, Gao and McCarthy[235] in 2007 published a paper "*How Wenzel and Cassie were wrong*", questioning the validity of both the Wenzel and Cassie–Baxter approaches. They argued that the contact line, and not the contact area, is important in interpretation of the advancing, receding and the contact angle hysteresis. The contact angles are governed by an activation energy, which must be overcome to move the three-phase contact line from one metastable (or stable) state to another. The significance of analyzing the three-phase contact line region in which surface forces operate instead of total surface area under the liquid was well recognized in the past.[236–238]

According to Gao and McCarthy,[235] the contact area is valid as reflected by "ground-state energy of contact line and the transition states between" the subsequent contact lines. A similar conclusion was drawn earlier by Extrand[239] for chemically heterogeneous surfaces. Also work by Drelich[237] on chemically heterogeneous surfaces and by Moulinet *et al.*[238] on rough surfaces pointed to the same need of analyzing the shape and contortion of the three-phase contact line.

The statement of Gao and McCarthy was based on experimental results obtained from three differently prepared two-component (hydrophilic–hydrophobic) surfaces. It was a stimulus to a hot discussion that rolled over Langmuir journal putting forward pro and con arguments.[240–244] Nosonovsky[240] derived generalized forms of Wenzel and Cassie–Baxter equations concluding that Wenzel's equation is valid if for a rough surface r = const. However, for a randomly rough surface, a generalized Wenzel equation should be applied, where r is a function of x,y coordinates:

$$\cos\theta_{\text{rough}} = r(x,y)\cos\theta \tag{13}$$

$$\text{where}: r(x,y) = \sqrt{\left(1 + \left(\frac{dz}{dx}\right)^2 + \left(\frac{dz}{dy}\right)^2\right)}$$

The generalized Cassie–Baxter equation for a composite surface can be expressed in a similar way:

$$\cos\theta_{\text{C–B}} = f_1(x,y)\cos\theta_1 + f_2(x,y)\cos\theta_2 \tag{14}$$

Here $f_1 + f_2 = 1$ and θ_1 and θ_2 are contact angles corresponding to the two components, *i.e.* air and solid. According to Nosonovsky the generalized forms of Wenzel and Cassie–Baxter equations apply to the surfaces whose protrusions and/or heterogeneities are small in comparison to the size of the liquid/vapor interface. Because most superhydrophobic or superhydrophilic surfaces possess multiscale protrusions and valleys, the use of the classical Wenzel or Cassie–Baxter equations is not straightforward as the solid area wetted by liquid is difficult to determine. If the surface roughness is present under the droplet but is absent in the triple contact line, like probably happened in the work of Gao and McCarthy,[235] then Young's equation applies instead of classical Wenzel or Cassie–Baxter, as stated by Nosonovsky.[240]

Then Panchagnula and Vedantam[241] concluded that the Cassie–Baxter equation is correct if the appropriate surface area fraction is taken into account, *i.e.*, the fraction value of surface areas seen by the contact line during its advancement. Gao and McCarthy[242] replied that the Wenzel and Cassie equations "*should be used with knowledge of their faults*" and that they had considered the contact line instead of the area fractions in earlier published papers, which promoted an understanding of the contact angle hysteresis, the lotus effect, and hydrophobic surfaces.[243,244]

McHale[245] put forward the question: "*Cassie and Wenzel: were they really wrong?*" and gave the answer that these equations can be used if the surface fraction and the roughness parameter appearing therein are taken as global parameters of the surface and not as those defined for the contact area of the droplet. According to him the local form of these equations "*allows patterning of the surface free energy*". In the case of a superhydrophobic surface the apparent contact angle results from minimization of the surface free energy by small displacements of the contact line. If the droplet penetrates the valleys then the Wenzel wetting mechanism occurs.[245] Later Whyman *et al.*[246] published "*rigorous derivation of Young, Cassie–Baxter and Wenzel equations*". They presume free displacement of the triple contact line and related the potential energy barrier to advancing and receding contact angles. This energy barrier is defined by the liquid adhesion and the solid roughness. Hence, a larger energy barrier causes larger contact angle hysteresis. Moreover, the derivation predicts low contact angle hysteresis for low contact angle values. However, in a broad range of the contact angles (50–140°) the contact angle hysteresis does not depend on the equilibrium contact angle, which is not the case for superhydrophobic surfaces. Also, except for very small droplets, the droplet volume does not determine the contact angle hysteresis. However, a larger contact angle hysteresis can be expected for a liquid whose surface tension is lower.[246]

Further, Marmur and Bittoun[247] demonstrated theoretically that both the Wenzel and Cassie equations are good approximations of contact angles on imperfect surfaces but it should be recognized that they are valid when the size ratio of the liquid drop to the wavelength of roughness or chemical heterogeneity is sufficiently large. They also showed that local considerations of the shape and length of the contact line and global considerations involving the interfacial area within the contact line do not contradict but complement each other.[247]

Recently, also Erbil and Cansoy[248] tested the validity of Cassie–Baxter and Wenzel equations to evaluate contact angles on 166 samples having patterned superhydrophobic surfaces (square and cylindrical pillars). They have used literature data recently published in eight papers. It was possible to calculate the roughness parameter from Wenzel's equation and the fraction of the water/solid contact surface under the droplet to the total projection of the droplet base. Then they compared the calculated values with the experimental ones obtained from the contact angles measured on flat and rough surfaces, respectively. They found that the Wenzel equation was wrong for most of the tested samples, *i.e.* 74% for cylindrical and 58% for square pillars. Moreover, for the rest of the samples significant deviation from the prediction of the Wenzel equation was also high (68%) and it was not thought to be caused by contact angle measurement errors. In the case of the Cassie–Baxter equation the authors have found disagreement in 65% of samples with cylindrical-pillar patterned surfaces and 44% of samples with square-pillar patterned surfaces. Also deviations from theoretical Cassie–Baxter contact angles were large for most of the samples. These results show that both Wenzel and Cassie–Baxter equations give a more qualitative than quantitative evaluation of the relationship between the contact angles on rough and flat surfaces and still the exact mechanism of rough surface wetting is open for further studies. Also molecular dynamics simulation results obtained by Leroy and Muller-Plathe[249] for a nanometre-scale rough graphite showed that Wenzel's theory fails "*to predict even qualitatively the variation of the solid–liquid surface free energy with respect to the roughness pattern.*" However, for the Cassie wetting state the solid–liquid surface free energy could be well predicted from the Cassie–Baxter equation. Similar testing on real randomly coarse surfaces has not been carried out yet and results could shed more light on the applicability of the Wenzel and Cassie–Baxter models to many surfaces of practical significance.

Interpretation of the experimental contact angles on rough substrates is always difficult because of the apparent pinning of the contact line on defects such as edges of asperities, causing departure from the Wenzel assumptions whether in terms of surface area or contact line length.[250,251] Both shape and sharpness of roughness features and their edges affect pinning of the contact line as is concluded from a diligent experiment with posts of different shapes performed by Oner and McCarthy.[252]

Lately Chibowski[253] suggested to use water (and other probe liquids as well) contact angle hysteresis for characterization of solid surface wetting properties *via* calculation of its apparent surface free energy,§§ γ_s^{tot}.[50,254–256] The energy can be calculated from the advancing θ_{adv} and receding θ_{rec} contact angles of one liquid only whose surface tension is γ_l. The equation reads:

$$\gamma_S^{tot} = \frac{\gamma_l(1+\cos\theta_{adv})^2}{(2+\cos\theta_{rec}+\cos\theta_{adv})} \tag{15}$$

The general feature of the apparent surface free energy as a function of the contact angle hysteresis (CAH) relationship is the decrease in energy with increasing hysteresis. The relative decrease of the apparent surface free energy is strongly sensitive to the advancing contact angle value. With increasing its value the apparent surface free energy drastically decreases even if the contact angle hysteresis is the same. For example, for $\theta_{adv} = 120°$ and CAH = 10° the decrease in the apparent surface free energy amounts to 13.6% in comparison to its value at zero hysteresis. However, if θ_{adv} amounts to 170°, with the same hysteresis, the energy decreases as much as nearly 60%. Of course, the absolute value of the apparent surface free energy decrease is large in the former case, *i.e.*, from 18.2 to 15.7 mJ m^{-2}, in comparison to the decrease in the latter case, *i.e.*, from 0.55 to 0.22 mJ m^{-2}.[253] These results also show differences between the two mechanisms of the wetting process, *i.e.*, suspended or collapsed drops, for hydrophobic and superhydrophobic surfaces.

9. Methods of preparation of superhydrophilic and superwetting surfaces

Most solids are naturally rough; however, their roughness is usually insufficient to reinforce a superhydrophilic state of the

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§§ Apparent surface free energy is an imaginary energy calculated based on apparent contact angles.

material surface. Although, in theory, any natural or synthetic material could be converted to one with superhydrophilic surface by chemical treatment and mechanical roughening or converted to sub-microscopic particles and then deposited to form a superhydrophilic coating, only a few materials have been explored for this approach. Among inorganic materials, titanium oxide (TiO_2)[187–190,192,193,199] and zinc oxide (ZnO)[191,193,257,258] are frequently studied because of their photoinduced self-cleaning capability. Also, silica (SiO_2)[188,259–265] is well studied due to its hydrophilicity and availability at a low price. Films of nanoparticles are often deposited on substrates from solutions/suspension,[188] ink-jet printing,[199,200] by a sol–gel technique,[187,190] spin coating[189,190] or through sputtering.[257] Sub-microscopic structures grown from solutions,[258,266] through lithographic[195] and electrochemical[198] techniques, are also used.

Polymers are also attractive materials for superhydrophilic coatings but their surfaces typically require oxidation. Improvement in hydrophilicity of polymer surfaces, as discussed earlier, can be obtained with many techniques that change surface chemistry such as the surface irradiation using γ-rays[113] or ion irradiation,[186] electron beam,[113] plasma[267] and corona treatment.[116,268,269] In order to make the polymer superhydrophilic the treatment must also have an effect on surface roughness or the chemical treatment must be performed in conjunction with surface roughening.

In recent years, coatings with switchable wetting properties have attracted interest from many research groups.[270] Several coatings showing a transition from superhydrophobic to superhydrophilic states were demonstrated.[184,191,202,205,271] This has been accomplished for films obtained by the sol–gel process, for example upon heating,[187,271] as well as by an electrochemical method (aluminium oxidation)[198] or coatings.[185,189,190,192,194,197,199,204,272] For example, transformation or even reversible transformation, depending on the treatment, of carbon nanotubes or buckypaper from superhydrophilic to superhydrophobic can be achieved by heating in vacuum, UV radiation or ozone treatment.[205] Zhang *et al.*[206] obtained micro–nanostructured nylon 6,6 whose as-formed surface was superwetting but after treatment with formic acid and ethanol and then dipping in paraffin wax solution in ethyl ether and drying, reversed to superhydrophobic. A reversible superhydrophilic to superhydrophobic WO_3 nanostructured film on alumina or tungsten substrates was produced by Gu *et al.*[202] The superhydrophobic film was obtained by covering the surface with *n*-dodecanethiol from its solution in ethanol, while the superhydrophilic surface was obtained by etching it with sodium dodecylbenzene sulfonate in concentrated HNO_3 solution.

10. Applications of superhydrophilic and superwetting surfaces

10.1. Anti-fogging surfaces

The need for anti-fogging surfaces arises in response to the challenge of visualization under high humidity. Swimming goggles offer an obvious example for such a scenario. Since the relative humidity is a strong function of temperature, the vapor can easily reach its saturation limit due to the temperature fluctuation or at a relatively cold solid surface, such as a lens or transparent wall to see through. As a result, significant condensation in the form of tiny droplets can be induced. The originally transparent solid surfaces will then fog and lose their optical clarity. In recent years, the necessity of anti-fogging surfaces has been highlighted by micro- and nanofluidic applications such as visualization of two phase flow in the cathode microchannels of proton electrolyte membrane fuel cells.[273] Similar challenges will also be encountered when stagnant multiphase environments in microreactors (*e.g.*, for cell cultivation[274]) need to be visualized. Anti-fogging surfaces can also find applications in our daily life. When a food item is packaged and displayed in a refrigerated cabinet, the relative humidity inside the package increases due to the decrease of temperature. Consequently, water tends to condense on the inner surface of packages, which, if treated to be anti-fogging, can enhance the visual displacement of the packaged items.

A superhydrophilic surface can prevent fog because water spreads on the rough hydrophilic surface to form a thin film instead of droplets. Such an effect can be easily illustrated by placing a piece of superhydrophilic polyester film on top of a cup filled with hot water.[275] As Fig. 4 shows, the plasma-treated superhydrophilic polyester film (right side) remained clear due to the formation of a continuous water film. As a comparison, the untreated polyester film (left side) was covered by water droplets and fogged after several minutes. Recent results[276] also revealed that similar plasma treatment can also generate superhydrophilic "nanoturf" surface with anti-reflection properties. It is reported that optical transmittance of a nanoturf surface is enhanced up to 92.5% as compared to a flat PUA surface (89.5%).[276]

It is noted that the superhydrophilic treatment is different from traditional anti-fogging coatings widely used for swimming goggles and eyeglasses. The latter usually employs various surface coatings to make the surface hydrophobic, which tends to have low adhesion with the tiny water droplet formed on it. Such hydrophobic anti-fog surfaces are usually more durable than the superhydrophilic surfaces that can be obtained by existing technology. However, a coating approach might be undesirable in many conditions, such as inside a microchannel. The safety of those chemical agents for biomedical samples and food is questionable especially when the surface is subjected to environments of high temperature and high humidity (*e.g.*, pasteurization process). Other concerns of hydrophobic anti-fog coatings are their efficacy when a polymer film is extruded (process temperature: 200–300 °C), the cost of the chemicals and the relatively small area it can be uniformly applied on.

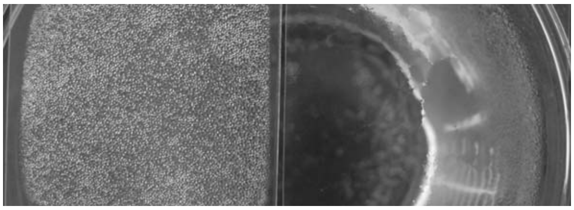

Fig. 4 Condensation and optical clarity of polyester films under high relative humidity. Left side: untreated polyester film is fogged. Right side: plasma-treated superhydrophilic polyester film retains optical clarity (reprinted from ref. 275 with permission).

10.2. Bio-fouling and its prevention/release

The continuous thin water film formed on a hydrophilic or superhydrophilic surface has a profound impact on the surface's interaction with molecules and microorganisms, including biofouling and biocompatibility (detailed in Section 10.3).

In marine engineering, fouling has mainly been used to describe the growth of microorganisms, algae, plant, *etc.* on a surface (*e.g.*, of a ship) immersed in seawater. Biomedical devices can also be subject to fouling *via* a deposit of cells and biomolecules (*e.g.*, proteins and DNAs). Fouling usually changes the original property of the surface negatively and significantly impacts the performance of the device or equipment. It is preferable to avoid (or at least slow down) or reverse biofouling, with strategies known as anti-fouling and fouling-release, respectively.[277] Biocides, such as a tributyltin moiety (TBT), have been widely used in the anti-fouling coating of marine vessels.[278] The concerns on environmental impact, as well as the need for biomedical applications, are driving the development of non-toxic, anti-fouling and fouling-release methods, such as microtopography to mimic the surfaces of shells and scales of marine life.[279–281]

Surface chemistry has also been known as a strong factor to affect fouling and its prevention/release. Extensive work by Baier and co-workers since the 1960s has led to the establishment of a predictive curve, as Fig. 5 shows, to show the relationships between the critical surface tension of a solid surface and the degree of biological fouling retention.[282] It is understood that fouling is such a complex issue that it cannot be sufficiently explained solely by surface energy or contact angle. However, the Bier curve has been proven to be an effective means to indicate the relative tendency of fouling in many cases, including blood fouling of biomedical devices or implants and bio-fouling of marine vessels.[282] Of particular interest has been a region with a relatively low surface energy of 22–24 mN m^{-1}, known as *theta surfaces*, which require minimal energy to detach biofilms. As *theta surfaces* are fouling-release instead of anti-fouling surfaces, external forces (*e.g.*, flow) and intervention are required to periodically remove the already fouled surfaces. It is interesting to look at the end with very high surface energy, or the hydrophilic part of the curve. A trend is clearly seen that for high-surface-energy materials, the degree of fouling actually decreases with surface energy. This can be explained by the strong affinity between the surface and water molecules, which establishes a barrier to prevent interaction between the fouling agent and the surface and thus delays the fouling. Indeed, recent work by Meng's group has shown significant reduction of fouling by fluorescein and fluorescent proteins after the surfaces are treated to be superhydrophilic.[283] It should be noted that such results have been obtained in a relatively short period (30 min incubation time) with static liquid. They are thus mainly intended for applications such as micro total analysis systems (μTAS) and not necessarily for long-term prevention and release of biofouling.[283] The difference in short-term and long-term[284] fouling behaviors of superhydrophilic and hydrophilic surfaces can be attributed to the quick degradation of hydrophilicity.

10.3. Other applications in the biomedical field

Hydrophilic coatings have been used in the medical field for the last few decades, for example in catheters, guide wires, and other vascular access devices for fertility, contraception, endoscopy, and respiratory care. Polyvinylpyrrolidone, polyurethanes, polyacrylic acid, polyethylene oxide, and polysaccharides were the main polymeric components in hydrophilic coatings. Reduction in friction was the main goal in the design of hydrophilic coatings. Recently, these coatings are also moving toward anti-fouling, antimicrobial and/or biologically active surfaces that perform tasks other than imparting lubricity. Also superhydrophilic coatings attracted interest among biomedical engineering research teams. Unfortunately, many claims of superhydrophilic surfaces or coatings do not comply with our definition presented earlier in this paper, as well as in our previous note.[158] For this reason, we remind our readers that flat surfaces with strong affinity to water should be simply called hydrophilic. We follow this definition in reviewing recent research activities in improving biocompatibility and affinity to water of implant materials.

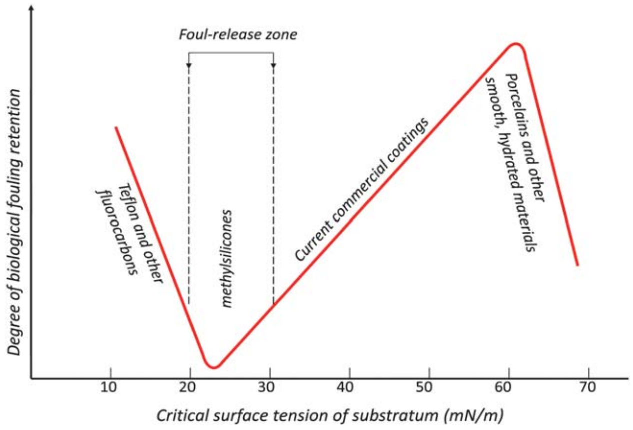

Fig. 5 Baier curve shows a descriptive correlation between the critical surface tension of the surface with the degree of bio-fouling retention (redrawn based on the figure in ref. 282).

Improving hydrophilicity of polymeric bio-implants. Biomedical applications of polymers include vascular grafts, heart valves, artificial hearts, catheters, breast implants, contact lenses, intraocular lenses, components of extracorporeal oxygenators, dialyzers and plasmapheresis units, coatings for pharmaceutical tablets and capsules, sutures, adhesives, and blood substitutes.[285] Stents, lenses, catheters, and implants require biologically non-fouling surfaces to which proteins, lipids and cells do not adhere. Both catheters and lenses are made hydrophilic, although for different purposes. Catheters and guidewires require low friction (coefficient of friction of 0.3 or less) so they are easily maneuvered within the patient's vasculature.[286,287] Hydrophilic coatings were found to provide better lubricity compared to hydrophobic coatings.[287,288] Lenses must be wetted by tear fluid to move relatively freely on the eye, providing wearer comfort.[289,290] The applied research on surface modification of contact lenses is substantial[288,291–295] and mostly deals with making the surface of polymer hydrophilic.

Contact lenses were introduced into the field of vision correction after discovery of highly oxygen permeable silicone hydrogels that satisfy the metabolic needs of the cornea, maintain its physiological health, and can be worn continuously for several days.[296,297] However, due to the hydrophobicity of silicone hydrogels they require hydrophilic coatings for improved wettability with tear fluid, wearing comfort and biocompatibility. Contact lenses, when inserted into the eye, accumulate proteins and other tear film components to which bacteria can adhere threatening adverse clinical events.[298] Advanced contact lens coatings are not only hydrophilic but also have low biofouling characteristics. Chemical modifications that create low-fouling surfaces have been the area of intensive research not only in the field of vision correction but also in biomedical applications in general. Surface coatings included neutral hydrophilic polymers such as polyacrylamide and poly(ethylene oxide) (PEO),[299] phospholipids,[300] dextran,[301] pullulan,[302] and others.[303,304] PEO has been the most popular polymer.[304,305] Recently, Shimizu *et al.*[306] synthesized hydrophilic silicone hydrogels from 2-methacryloyloxyethyl phosphorylcholine (MPC) and bis(trimethylsilyloxy)-methylsilylpropyl glycerol methacrylate (SiMA) by controlling the surface enrichment of MPC units. New silicone-based hydrogel maintains high oxygen permeability and the MPC units at the surface are responsible for low protein adsorption.

Titanium-based biomaterials. Due to their high biocompatibility, elastic modulus that closely matches human bone, good ductility, fatigue and tensile strength, titanium (Ti) and Ti-based alloys are very popular for orthopedic implants.[307,308] The high biocompatibility of Ti-based biomaterials is attributed to a surface oxide layer. In fact, almost all Ti-based implants undergo some sort of anodization, electropolishing, passivation and/or other treatment, used to control the type of oxide layer, its thickness and surface topography.[309] It is only in the last couple of years that photoinduced hydrophilic and photocatalytic cleaning properties of titanium oxides[18] have been explored for applications in the area of biomaterial implants. There is sufficient evidence to support the removal of organic contaminants[310] and bacteria[311] adsorbed on a TiO_2 surface by the photooxidization process. Such self-cleaning is believed to occur particularly in the case of TiO_2 films that exhibit hydrophilicity.[310] Self-sterilization capability of TiO_2 surfaces, ignored in the past, will likely be explored by the biomedical industry sector in the near future.

Changes in the bioactivity of titanium and chromium–cobalt alloy surfaces during their aging and exposure to the ultraviolet (UV) light treatment were recently studied.[312,313] The study conducted uncovered a time dependent biological degradation of biomaterials, which was restored by UV phototreatment. The restoration was more closely linked to hydrocarbon contaminant removal than the hydrophilicity induced during UV treatment. These two effects are inter-related because the surface of implant materials has enhanced affinity to water when free of organic contaminants. However, surface OH groups are needed to make the interaction strong through hydrogen bonding.[309]

More recently, Ogawa *et al.*[314,315] demonstrated that UV light treatment of TiO_2 is effective in converting implant material surfaces to hydrophilic ones, and this conversion enhanced osteogenic environment. They found that the number of rat bone marrow-derived osteoblasts cultured and attached to hydrophilic surfaces was substantially greater than on untreated TiO_2 surfaces. Adhesion of a single osteoblast was also enhanced on UV-treated TiO_2 with virtually no surface roughness or topographical features. Osteoblasts on UV-treated TiO_2 surfaces were larger and with increased levels of vinculin expression and focal contact formation, although the density of vinculin or focal contact was not influenced by hydrophilicity.

The same research group also found that TiO_2 with restored hydrophilicity has higher albumin and fibronectin protein adsorption, human osteoblast migration, attachment, differentiation, and mineralization than untreated TiO_2 surfaces even if untreated surfaces are freshly prepared.[316] Time-related degradation of TiO_2 bioactivity was found to be significant in regular storage conditions, which affected recruitment and function of human osteoblasts. However, UV treatment restored and often enhanced TiO_2 surface bioactivity.

Ogawa *et al.*[314–316] also demonstrated that photofunctionalization of materials can be accomplished through a coating process. Non-Ti biomaterials can be coated with TiO_2 particles which are effective in developing functional biomaterials and improving their bioactivity.

Superhydrophilicity for growing bone-like structures. The new generation of orthopedic implants and tissue engineering scaffolds is explored through accurately designed 3D structures of materials.[317] Efforts which are underway concentrate on improving the bioactivity and biocompatibility of the core materials used in orthopedic applications such as Ti-based alloys[318–321] and polymers.[319,321–323] Surface treatments include coating with biomimetic calcium phosphate (CaP) bioactive layers or chemical modifications to enhance hydroxyapatite formation on the biomaterial surface when in contact with the living bone. Fig. 6 shows examples of porous, superhydrophilic and biocompatible coatings of calcium phosphate produced at Michigan Tech.

Biological properties of the coated implants and scaffolds depend not only on the chemical composition of the coating but also on its structure. The ideal coating should resemble the structure of natural bone, which is favorable for cell anchoring and cell culture, and should be a run-through 3D structure. Hydroxyapatite and tricalcium phosphate coatings accelerate osteoblast cell attachment and proliferation, reducing the inhalation process and enhancing hard tissue integration.[318–321] Hydrophilicity was found to favor deposition of Ca-based bioactive coatings on biomaterials. Recently, Lai *et al.*[317] used hydrophilic–hydrophobic patterned templates to fabricate structured octacalcium phosphate films on bioactive TiO_2 nanotube surfaces. By controlling wettability patterns, desired hierarchically structured OCP films were manufactured.

Wu *et al.*[324] produced a 3D complex-shaped microporous titanium-based scaffold with superhydrophilic surface characteristics *via* a facile low-temperature alkaline-based hydrothermal process. They achieved a hierarchical structure on the nano- and micro-scale that closely resembles the structural organization of a human bone, and these submicroscopic structures are primarily responsible for the superhydrophilicity of the scaffold. Due to good wettability of material surfaces by alkaline solutions used in the hydrothermal process, it can penetrate the entire exposed scaffold surface despite the complex topographies of the 3D porous scaffold.

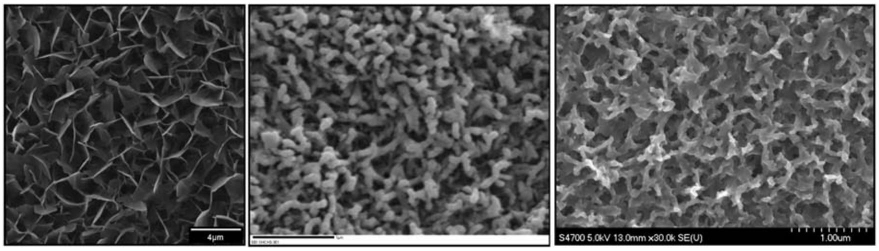

Fig. 6 Examples of calcium phosphate biocompatible (superhydrophilic) structures produced on a Ti_6Al_4V substrate (left),[318] a monolayer of thiol of mixed OH and CH_3 end functionality (middle) and a monolayer of thiol with COOH end functionality (right).[350]

Biomimetically grown structures favor the formation of a smooth junction between the bone tissue and scaffold and benefit the long-term fixation of the scaffold. The enhancement in hydrophilicity of TiO_2 is closely related to the formation of highly crystallized anatase TiO_2,[311,325] which can be promoted by increasing the conversion voltage during anodic oxidation or subsequent annealing.[325] Although rutile is a more stable titanium oxide, anatase is considered to be more advantageous for medical applications. Anatase adheres more strongly to Ti metal and absorbs more PO_4^{3-} and OH^- ions in the body fluid, ions which favor formation of a bone-like apatite structure.[326,327]

Bioactive and superhydrophilic TiO_2 coatings were prepared on PET film substrates using dip coating methods and subsequent glow discharge plasma treatment by Pandiyaraj *et al.*[328] The chemical and morphological characteristics of the cleaned and rough TiO_2 coatings induced the growth of bone like apatite layers from simulated body fluid solution.

10.4. Enhanced boiling heat transfer

Known as a most efficient cooling approach, boiling has been employed in a broad range of power generation and thermal management devices, such as nuclear power plants,[329] refrigeration,[330] cooling of electronics[331] and chemical reactors.[332] Boiling heat transfer can also be significantly affected by surface wettability. Fig. 7 shows a boiling curve which correlates the heat flux with wall superheat. Nucleate boiling starts from point A, with vapor bubbles forming on the overheated surface. The nucleate boiling continues to fully develop from B to C. At point C, the heat flux eventually reaches its maximum value, known as critical heat flux (CHF). Beyond CHF, a continuous vapor film is formed as an effective thermal insulation layer between the coolant and the device surface. Further heating beyond CHF will lead to a dramatic increase of wall temperature and thus device failure. Therefore, CHF marks the maximum heat flux that can be provided by a boiling-based cooler.

It is intuitive that the continuous water film formed on a hydrophilic or superhydrophilic surface can delay the formation of a vapor film in boiling and thus improve CHF. Experimentally, vertically aligned nanoforests of hydrophilic/superhydrophilic nanorods,[333] nanowires[334,335] and CNTs[336] have shown the potential to significantly improve boiling heat transfer. For example, both CHF and heat transfer coefficient (HTC) have been improved by more than 100% by this method.[334] Such improvements have been attributed to the dramatically increased density of nucleation sites, high surface tension forces of superhydrophilic nanostructures for pumping in fresh liquid and the cavity stability provided by the nanopores.[333,334] It has also been shown that a surface with mixed hydrophilic and hydrophobic micropatterns can enhance pool boiling to almost the same degree. For example, 65% and 100% improvements on CHF and HTC respectively[337] have been achieved with a hydrophilic network decorated by hydrophobic islands of ~100 μm. In spite of the relatively simple configuration of the surface, the results have been convincingly explained by the fact that the hydrophilic network can prevent formation of the vapor film by attracting liquid while the hydrophobic region can promote nucleation and help to remove gas bubbles efficiently.[337]

10.5. Other applications

Many other applications of hydrophilic and superhydrophilic surfaces are not included in the above discussions. For example, hydrophilic modification has been long known as an effective way to improve adhesion.[338,339] It has also been explored recently to decrease the impedance of neural microelectrode arrays.[340] Switchable wettability may find applications in reconfigurable microfluidic devices, such as droplet-based lab-on-a-chip by electrowetting-based actuation,[341,342] liquid microlenses[343] and arrayed optics.[344] The wettability switching mechanism has been

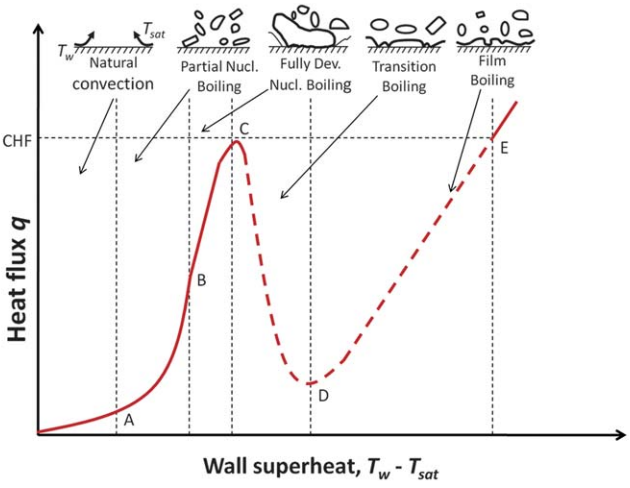

Fig. 7 A boiling curve illustrating the formation of nucleation and the correlations between wall superheat and heat flux (prepared based on ref. 351).

comprehensively reviewed recently.[345] More examples as well as their preparation methods can be found in Section 9 of this paper. Surfaces may exhibit tunable wettability from superhydrophilic to superhydrophobic, especially those coated with conductive polymers[346] or nanomaterials, such as ZnO nanorods,[347] carbon nanotubes[348] and graphene.[349] The research on extreme wettability is a highly dynamic field. It can be expected that more applications of the superhydrophilic surface will be developed in the foreseeable future.

11. Conclusion and outlook

We define superhydrophilic surfaces, and coatings, as rough (and sometimes porous) surfaces (coatings) of materials having affinity to water greater than to nonpolar air. Water spreads completely on these rough surfaces. Flat and smooth surfaces of hydrophilic materials, on which water spreads completely (even if hydrophilicity results from photoinduced or other cleaning), do not belong to this category. The vast majority of materials could be considered hydrophilic due to a polar-type contribution to the solid–water interactions and therefore there is a need to group them under different categories, with different degrees of hydrophilicity. The literature lacks such a classification, posing challenges for researchers to fill this gap of science. In this review paper, using the values of (advancing) water contact angles (θ) we have proposed to classify smooth solid surfaces as hydrophilic ($\theta \cong 0°$), weakly hydrophilic ($0 < \theta < (56–65°)$), weakly hydrophobic ($(56–65°) < \theta < 90°$) and hydrophobic ($90° \leq \theta < 120°$). The exact cut-off in the contact angle value separating weakly hydrophilic from weakly hydrophobic materials needs to be determined in future research. Another challenge ahead relates to the meaning and interpretation of water contact angle with zero value, if such a contact angle can be measured experimentally.

The research on superhydrophilicity has emerged in the last few years, with a noticeable increase in the number of publications since 2000, and will certainly attract the attention of many research groups in the years to come. In spite of the young age of superhydrophilicity research, many research activities from the past could be considered as a solid foundation for this new subdiscipline. For example, surfaces of hydrophilic materials were roughened in the past to improve adhesion in composites, biocompatibility in implant devices, or simply to enhance spreading of liquids, even so these activities were not linked yet to superhydrophilicity.

The progress on fabrication and characterization of superhydrophilic surfaces and coatings, along with understanding of liquid spreading on such materials, is driven by a broad application of superhydrophilic surfaces in products with anti-fogging screens, windows and lenses, anti-fouling coatings, microfluidic devices, biocompatible implant devices, coatings for enhanced boiling heat transfer, foils for food packaging, and many others. There is already a wide spectrum of products available on the market whose design was inspired by the superhydrophilic phenomenon. These products include anti-fogging mirrors for bathrooms and cars, shields of helmets for motorcycles, swimming goggles, lenses of eyeglasses, and safety eyeglasses and shields. Because the research on superhydrophilicity is a highly dynamic field, more interesting products with superhydrophilic surfaces will be developed in the near future.

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