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Superhydrophilic and Superwetting Surfaces: Definition and Mechanisms of Control

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The term *superhydrophobicity* was introduced in 1996 to describe water-repellent fractal surfaces, made of a hydrophobic material, on which water drops remain as almost perfect spheres and roll off such surfaces leaving no residue. Today, *superhydrophobic surfaces* are defined as textured materials (and coatings) on (nonsmooth) surfaces on which water forms contact angles 150° and larger, with only a few degrees of contact angle hysteresis (or sliding angle). The terms *superhydrophilicity* and *superwetting* were introduced a few years after the term *superhydrophobicity* to describe the complete spreading of water or liquid on substrates. The definition of superhydrophilic and superwetting substrates has not been clarified yet, and unrestricted use of these terms sometimes stirs controversy. This Letter briefly reviews the superwetting phenomenon and offers a suggestion on defining superhydrophilic and superwetting substrates and surfaces.

Introduction

Over the last several decades, surfaces of materials have been commonly classified as *hydrophobic*, with water contact angles larger than 90° ($\theta > 90^\circ$), and *hydrophilic*, with contact angles of $\theta < 90^\circ$ (discussion on the validity and accuracy of this definition is beyond the scope of this note). The term *superhydrophobicity* was introduced in 1996 by Onda et al.^{1,2} to describe water-repellent fractal surfaces, made of a hydrophobic material, on which water drops remain as almost perfect spheres and roll off such surfaces leaving no residue. Superhydrophobic surfaces are now defined as textured materials (and coatings) on (nonsmooth) surfaces on which water forms contact angles 150° and larger, with only a few degrees of contact angle hysteresis (or sliding angle), $< 5\text{--}10^\circ$.³ On a contrary, there is no clear definition of *superhydrophilic* and *superwetting* surfaces. For example, in a recent review, Shirtcliffe et al. wrote:⁴ "... This raises the question of the definition of a *superhydrophilic* (or *superwetting*) surface, since roughness is not required to create film-forming surfaces even for water. However, creating a film where one would not otherwise be created be regarded as *super-wetting*..." This note briefly reviews the superwetting phenomenon and offers a suggestion on how superhydrophilic and superwetting substrates and surfaces could be defined.

Origin of Superhydrophilicity and Superwetting Terms

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), contact angles of 150–174° demonstrated for a large number of superhydrophobic substrates and coatings could only

be achieved through manipulation of surface roughness, texture, and/or porosity.^{3,5–7} Manipulation of surface texture to achieve water repellency and self-cleaning has been inspired by many biological materials.^{8,9} Engineering of 2D (two-dimensional) and 3D structures has inspired fabrication of superhydrophilic (superwetting) surfaces as well.

The terms superhydrophilic and superwetting surfaces were introduced soon after the explosion of research on superhydrophobic surfaces, in response to demand for surfaces with exceptionally strong interactions to water and liquid, respectively.¹⁰ It is often assumed that the term superhydrophilic/superwetting substrate refers to one on which water/liquid spreads to zero or nearly zero contact angle.⁷

Water can spread out completely on just a few nonporous and smooth materials including glass,⁶ gold,¹¹ selected oxides (having OH groups on the surface),^{12,13} selected self-assembled monolayers with OH-based functionalities (OH, COOH, POOH),^{14–16} biological specimens,¹⁷ and then only if these materials are freshly prepared and/or their surfaces are carefully cleaned.^{6,18,19} These surfaces, though having a strong affinity toward water molecules, have been commonly recognized as hydrophilic. Their strong hydrophilicity is usually a short-lasting effect and airborne

(5) Pugno, N. M. *J. Phys.: Condens. Matter* **2007**, *19*, 17.

(6) Quere, D. *Rep. Prog. Phys.* **2005**, *68*, 2495.

(7) Feng, X. J.; Jiang, L. *Adv. Mater.* **2006**, *18*, 3063.

(8) Barthlott, W.; Neinhuis, C. *Planta* **1997**, *202*, 1.

(9) Neinhuis, C.; Barthlott, W. *Ann. Bot.* **1997**, *79*, 667.

(10) Fujishima, A.; Rao, T. N.; Tryk, D. A. *Electrochim. Acta* **2000**, *45*, 4683.

(11) Smith, T. J. *J. Colloid Interface Sci.* **1980**, *75*, 51.

(12) Gentleman, M. M.; Ruud, J. A. *Langmuir* **2010**, *26*, 1408.

(13) Harju, M.; Levanen, E.; Mäntylä, T. *Appl. Surf. Sci.* **2006**, *252*, 8514.

(14) Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

(15) Bain, C. D.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1370.

(16) Lee, T. R.; Carey, R. I.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 741.

(17) van Oss, C. J. *Interfacial Forces in Aqueous Media*; Marcel Dekker, Inc.: New York, 1994.

(18) Takeda, S.; Fukawa, M.; Hayashi, Y.; Matsumoto, K. *Thin Solid Films* **1999**, *339*, 220.

(19) Takeda, S.; Yamamoto, K.; Hayasaka, Y.; Matsumoto, K. *J. Non-Cryst. Solids* **1999**, *249*, 41.

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(1) Onda, T.; Shibuichi, S.; Satoh, N.; Tsujii, K. *Langmuir* **1996**, *12*, 2125.

(2) Shibuichi, S.; Onda, T.; Satoh, N.; Tsujii, K. *J. Phys. Chem.* **1996**, *100*, 19512.

(3) Roach, P.; Shirtcliffe, N. J.; Newton, M. I. *Soft Matter* **2008**, *4*, 224.

(4) Shirtcliffe, N. J.; McHale, G.; Atherton, S.; Newton, M. I. *Adv. Colloid Interface Sci.* **2010**, *161*, 124.

contaminants accumulating on the surface instantly reduce their affinity to water. Contact angles for water increase to a few tens of degrees as the result of surface contamination.^{18,19}

Titanium oxide (TiO₂) is known as a photocatalyst,²⁰ and TiO₂-based coatings are now used for antifogging and self-cleaning.²¹ This oxide exhibits behavior similar to that of many other oxide surfaces, with a water contact angle of a few tens of degrees.¹⁸ However, under UV illumination, photocatalytic self-cleaning combined with chemical and morphological transformation of the TiO₂ surface takes place,^{21–23} enhancing hydrophilicity gradually to what now is usually (and unfortunately) called the *superhydrophilic* state and facilitating the spread of water to a final contact angle of nearly 0°. ²⁴ The term superhydrophilic was probably used for the first time by Fujishima et al.,¹⁰ although the term of *superwetable* surface was already introduced by Onda et al.¹ However, the term superwetable referred to substrates in which the wetting characteristics have been enhanced through manipulation of substrate surface roughness.

In the following sections, the Wenzel and Cassie models describing contact angles on rough surfaces are briefly reviewed. We use these models to explain physical behavior of a liquid on rough and porous surfaces, although it should be recognized that both models have a limited practical significance. The Wenzel and Cassie equations were derived based on thermodynamic arguments and require the use of equilibrium contact angles that are almost never measured experimentally. It is a common practice to replace equilibrium contact angles with experimental advancing contact angles in interpretation of behavior of liquid on rough and porous surfaces using the Wenzel and Cassie equations. The reader should be aware, however, that for many rough surfaces advancing contact angle values can depart significantly from equilibrium ones. This departure is driven by the geometry and spacing of surface features and represents the three-phase system trapped in a metastable state.²⁵

Manipulation of Superwetting through Surface Roughening

Since the late 1990s, laboratories have searched for alternatives to TiO₂ and quickly recognized that materials having low contact angles could be converted to superwetting through a manipulation of their surface texture.^{26,27} The concept is not new as it dates back to 1936, when Wenzel proposed a new equation describing the effect of surface roughness on contact angle:²⁸

$$\cos \theta_0 = r \cos \theta \quad (1)$$

where θ_0 and θ are the macroscopic (apparent) and intrinsic (Young) contact angles measured on rough and flat surfaces of the same material, respectively, and r is the roughness factor defined as the ratio between actual and projected surface area of the substrate. The apparent (or macroscopic) contact angle is observed with the optical system, and the intrinsic contact angle is

(20) Takeuchi, M.; Sakamoto, K.; Martra, G.; Coluccia, S.; Anpo, M. *J. Phys. Chem. B* **2005**, *109*, 15422.

(21) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Nature* **1997**, *388*, 431.

(22) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Adv. Mater.* **1998**, *10*, 135.

(23) Sakai, N.; Wang, R.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *Langmuir* **1998**, *14*, 5918.

(24) Wang, R.; Sakai, N.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *J. Phys. Chem. B* **1999**, *103*, 2188.

(25) Boinovich, L. B.; Emelyanenko, A. M. *Usp. Khim.* **2008**, *77*, 619.

(26) Bico, J.; Marzolin, C.; Quere, D. *Europhys. Lett.* **1999**, *47*, 220.

(27) Bico, J.; Thiele, U.; Quere, D. *Colloids Surf., A* **2002**, *206*, 41.

(28) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988.

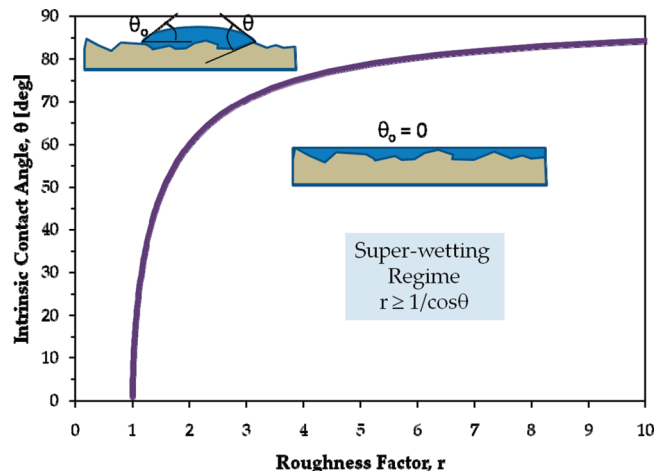


Figure 1. Minimum values of roughness factor necessary to promote complete spreading of liquid on a surface with varying Young's (intrinsic) contact angle as calculated with the Wenzel equation (eq 1).

the value characteristic to the material, defined by the Young equation. Both angles are considered to represent equilibrium contact angles of rough and flat surfaces of the same material.

The Wenzel equation (eq 1) predicts the increase in apparent contact angle with increasing roughness of hydrophobic material whereas roughness reduces apparent contact angle on roughened hydrophilic material. Since our attention concentrates on hydrophilic materials (and materials with enhanced affinity to wetting liquids), the hydrophobic rough substrates are excluded from further analysis.

Figure 1 shows the correlation between the Young contact angle (θ) and the minimum value of the roughness factor (r) that is necessary to promote complete spreading of liquid on the rough substrate, as per Wenzel's equation. It shows that, with a moderate roughening of the substrate surface, $r = 1.2$ – 2 , 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. The validity of Wenzel's equation was partially confirmed for several liquids on fractal surfaces.^{1,2} However, the results presented by Onda et al. revealed also the limitations of Wenzel's analysis of liquids behavior on extremely rough substrates, and we concentrate on one of the limitations in the following section.

Manipulation of Superwetting through Substrate Porosity

In many systems with low θ values, the zero apparent contact angle was not achieved in spite of large r values: $r = 2.6$ – 4.4 for fractal surfaces used.^{1,2} The effect was particularly clear for fractal surfaces made of alkylketene dimer with $r = 4.4$. It was later recognized that such surfaces should be treated more like porous materials.^{26,27} Spontaneous invasion of liquid inside the texture of porous materials takes place through capillary phenomenon, while the remaining liquid sits on the surface, making a patchwork of solid and liquid. The apparent contact angle for such a system (liquid on top of porous material) can be described by the following equation:

$$\cos \theta_0 = f_s(\cos \theta - 1) + 1 \quad (2)$$

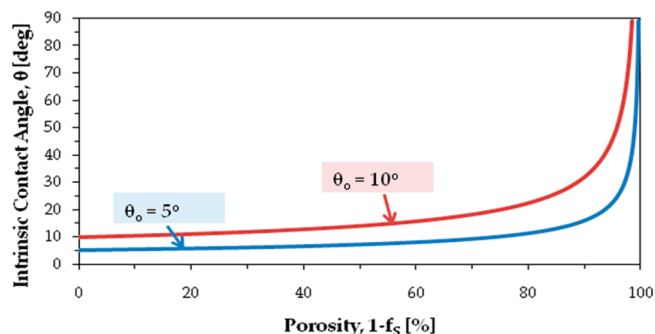


Figure 2. Minimum porosity in a textured substrate required to maintain 5° or 10° apparent contact angle, as per eq 2.

where f_s is the fraction of liquid in contact with the solid ($1 - f_s$ is the fraction of the textured surface that is filled with liquid).

Equation 2 predicts improvement in liquid spreading on porous materials (or coatings) through developed porosity. It also indicates, however, that liquid will not spread completely to a film unless the material is already perfectly wetted by this liquid. In practice, this problem can be overcome through the manipulation of porosity volume. If the porosity volume is comparable or larger than the volume of liquid used in the spreading test, θ_0 will drop to zero, as the entire liquid will be consumed for impregnating the porosity.

Previous literature suggests that, instead of a zero liquid apparent contact angle, a nearly zero contact angle is sufficient for the surface to be called superwetting or superhydrophilic.⁷

Figure 2 shows the calculated minimum amount of porosity, expressed in term of the fraction of the textured surface to be filled with liquid, necessary to maintain nearly zero apparent contact angle, 5° or 10°. The correlations clearly show that the porosity has a very strong effect on wettability characteristics of surfaces

having large or moderate intrinsic contact angles, $> 25\text{--}30^\circ$. The effect of porosity on materials having strong affinity to liquid, $\theta < 20^\circ$, is minimal. This suggests that roughening of such surfaces and maintaining Wenzel's criterion, as discussed earlier, is probably a more practical approach than making the surface highly porous.

Conclusion and Suggestion

Based on the literature reports published in the past decade, the primary prerequisite for a material or surface to be called superhydrophilic (superwetting) is that water (liquid) spreads on it completely (to a nearly zero apparent contact angle; not measurable accurately by optical systems, $< 5\text{--}10^\circ$) at material/product functioning conditions. Unfortunately, both nonporous and porous materials, having either smooth or textured surfaces, were sorted into this category. The physics behind liquid spreading on smooth and textured materials is different, and the same terminology should not apply to both groups of materials. For example, on smooth and clean surfaces, strong molecular interactions of water with surface functional groups dominate complete spreading. Such surfaces have been called hydrophilic in the surface chemistry literature for several decades, and the term superhydrophilicity should not apply to them.

It is suggested here that the term superhydrophilic (superwetting) materials only refers to those textured and/or structured materials (rough and/or porous) having a surface roughness factor (as defined in the Wenzel equation) larger than one, $r > 1$, on which water (liquid) spreads completely. Roughness enhances the spread of liquid, and capillary forces dominate wicking of liquid into the structure of textured materials. As a result, the common practical approaches in fabricating superwetting surfaces are through manipulation of surface texture, often accompanied by thorough cleaning and surface chemistry manipulation.