



## Review Article

# Hierarchical micro and nano structured, hydrophilic, superhydrophobic and superoleophobic surfaces incorporated in microfluidics, microarrays and lab on chip microsystems



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## ABSTRACT

Control of wetting properties at the extremes of wetting states (superhydrophilic and superhydrophobic) is important for many applications, such as self-cleaning, anti-fogging, anti-icing, and antibacterial action. While significant effort has been devoted to develop and characterize such open surfaces for various applications, their incorporation in sensors, microfluidics, and labs on chip, offers new functional devices and systems, and poses different requirements compared to open-area surfaces. In this paper, dedicated to the 30 year anniversary of Microelectronic Engineering, we aim to review the extreme wetting states of surfaces, their fabrication processes focusing on plasma processing technology, and their incorporation into devices and systems. We start with an introduction and terminology for superhydrophilic, superhydrophobic, and superoleophobic surfaces, and continue with a review of the fabrication of such surfaces by plasma processing. We then review how such surfaces are incorporated in microdevices and microsystems, and their applications. We address (a) Hydrophilic capillary pumps and superhydrophobic valves, (b) Drag reduction in superhydrophobic microchannels and slip length increase, (c) Superhydrophobic surfaces for droplet manipulation, applied to chemical and biological analysis, (d) Biomolecule adsorption control on nanostructured surfaces, and (e) Cell adhesion on such surfaces. Finally, we conclude with perspectives and challenges.

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## 1. Introduction and terminology

Control of wetting properties at the extremes of wetting states has acquired an increased interest for many applications, such as self-cleaning, anti-fogging, anti-icing, and antibacterial action. Such surfaces are usually structured at the micro and nano-scale and possess high or low surface energy. On one extreme lie superhydrophilic and hydrophilic surfaces, while on the other extreme superhydrophobic and superoleophobic surfaces are encountered. While significant effort has been devoted to develop and characterize such open surfaces for various applications, their incorporation in sensors, microfluidics and labs on chip, offers new functional devices and systems, and poses different requirements compared to open-area surfaces. In addition, it narrows the possible fabrication steps, so that compatibility with microsystem fabrication technologies is possible.

In this paper, we aim to review the extreme wetting states of surfaces, their fabrication processes focusing on plasma processing technology, and their incorporation into devices and systems.

We start with the definitions of super wetting states for which often multiple terms and some confusion may exist [1,2]. Most of the words are combinations of Greek or Latin roots with the following meanings: “hydro = water”, “oleo = elaiion = oil”, “philic = friendly, attracting”, “phobic = afraid of, repelling”, “motus = fear”, “amphi = both (i.e. water and oils for this application)”, “omni = all, everything”. We essentially agree with the classification and terminology proposed in [1], but we prefer to separate oils (typical edible oils have surface tensions larger than 30 mN/m) from lower surface tension liquids (e.g. alkanes). We keep the term oleophobic for oils, and the term omniphobic for all liquids including liquids of lower surface tension compared to oils, considering that “omni” is a root with stronger meaning encompassing all liquids, while “amphi” has a weaker meaning referring both to oils and water. Table 1 below summarizes the surface classifications and the terminology used for such surfaces. The reason for such detailed classification is that the lower the surface tension the more difficult it is to obtain a superamphiphobic state. In addition as discussed in [2], there are some counter-intuitive cases where a surface may be oleophobic, but not hydrophobic, hence the need for the prefix amphi or omni.

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**Table 1**  
Definitions of extreme wetting states.

State	Superhydrophilic	Superoleophilic	Hydrophilic	Oleophilic	Hydrophobic	Oleophobic	Omniphobic	Superhydrophobic	Superoleophobic	Superamphiphobic	Superomniphobic
Liquid	Water	Oils	Water	Oils	Water	Oils ( $\gamma > 30 \text{ mN/m}$ )	Oils and liquids with $\gamma < 30 \text{ mN/m}$	Water	Oils	Both water and oils	All, water, oils, and low surface tension liquids ( $\gamma < 30 \text{ mN/m}$ )
Static contact angle	$<10^\circ$	$<10^\circ$	$10^\circ < \theta < 90^\circ$	$10^\circ < \theta < 90^\circ$	$90^\circ < \theta < 150^\circ$	$90^\circ < \theta < 150^\circ$	$90^\circ < \theta < 150^\circ$	$>150^\circ$	$>150^\circ$	$>150^\circ$	$>150^\circ$
Hysteresis	na	na	na	na	$>10^\circ$ (sticky surface)	$>10^\circ$ (sticky surface)	$>10^\circ$ (sticky surface)	$<10^\circ$ (slippery surface)	$<10^\circ$ (slippery surface)	$<10^\circ$ (slippery surface)	$<10^\circ$ (slippery surface)

Fig. 1 shows the spectrum of contact angles obtained for drops sitting on a rough super-wetting or super-anti-wetting surfaces. On one hand completely wetted superhydrophilic/superoleophilic/superamphiphilic states exist on rough surfaces. On the other hand at the “phobic” side of contact angles various states are found, starting from those where liquid wets the rough elements (Wenzel states, or “sticky” hydrophobic states) and ending in the super-anti-wetting states with very high contact angles. It is clearly understood that liquid drops easily roll-off on such super-anti-wetting surfaces. A drop can slip on a surface in two ways: (a) by contacting only a small solid fraction of the nanostructured surface, while the air fills in the rest of the surface asperities (the so called Cassie-Baxter or “fakir” state), or (b) by sliding on an oil layer impregnating the surface asperities the so called SLIP mode (slippery liquid-infused porous surface) [3]. While we make note of the SLIP mode, we shall mostly focus on the “fakir” state, as it involves more demanding micro-nano-fabrication. Both modes enable complete control of droplet movement in droplet based microfluidics. However, similar advantages exist in open or closed microfluidics, when for example a slip boundary condition is applied, rather than the well-known no-slip boundary condition. In addition, the known strong relation of wetting properties to biomolecule/cell adhesion allows “intelligence” and complexity to be added in microfluidics by incorporation of such surfaces. We attempt here a review of such efforts.

## 2. Fabrication of nanostructured hydrophilic, superhydrophobic and superoleophobic surfaces

The theory, design, fabrication and characterization of such surfaces have received enormous attention in recent years. Several reviews have appeared for superhydrophobic surfaces. Examples of recent reviews include a review by Shirtcliffe et al. for polymeric surfaces [4], one by Celia et al. for the design and fabrication of superhydrophobic surfaces [5], one by Yan for the theoretical aspects of superhydrophobic surfaces, their biomimetic aspect, and their fabrication [6], another by Liu and Jiang [7] for bioinspired multiscale (hierarchical) structures, yet another by Yao et al. for self-cleaning and antireflective properties [8], and yet another by Grinthal and Aizenberg which reviews the SLIPS surfaces and applications [9]. We note that since water is a liquid with a large surface tension compared to other common liquids and oils, it is easy to achieve superhydrophobicity with a “modest” topography (e.g. small height topography, not necessarily hierarchical, with no overhang structures etc.) and an initially hydrophobic material without coating or a “modest” hydrophobic coating (i.e. with initial contact angles in the range  $90\text{--}105^\circ$ ). However, superoleophobicity, superamphiphobicity, and superomniphobicity are increasingly more difficult to achieve, as the surface tensions of oils and alkanes are low, and thus their spreading on the surface is easier. Nevertheless, great progress has

recently taken place for superoleophobic surfaces. Recent reviews on the topic include a detailed review by Liu et al. on design, fabrication and application of superoleophobic surfaces [10], a shorter review from the same group by Xue et al. focusing on superoleophobic polymers [11], one by Valipour et al. stressing applications [12], another by Bellanger et al. focusing on the physics and chemistry needed and on the theoretical background for such surfaces [13], yet another by Bae et al. which emphasizes the role of hierarchy on bioinspired structures [14], and yet another by Chu and Seeger for superamphiphobic surfaces [15].

In the above mentioned publications a panorama of fabrication technologies is reviewed and compared. One important technology for fabrication of such “smart” surfaces is plasma processing. This technology is most well suited for microsystems and labs on chip, as it is often a technology used in their fabrication, while it allows the creation of the whole spectrum of wetting regimes depending on the plasma chemistry used. Already, a few reviews have appeared on plasma technology for super-anti-wetting surfaces. Vourdas et al. [16], and Gogolides et al. [17] reviewed the work on plasma nanotexturing of polymers for superhydrophobicity and antireflectivity, Kylian et al. reviewed nanostructured, low-pressure, plasma deposited polymers [18], while Jafari et al. reviewed the plasma technology for superhydrophobicity [19].

### 2.1. Randomly nanostructured surfaces via plasma etching or deposition

Plasma technology – usually at low pressure – can be used in various modes, such as plasma etching, plasma deposition, and sputtering with inert gases. Plasma etching or sputtering of polymers with oxygen or noble-gas plasmas was found early-on to cause roughening of the polymers. Mora et al. [20] in 1988 observed that oxygen plasma treatment of Poly(tetrafluoroethylene) (PTFE) at a low pressure of 2 Pa created topographical and wetting changes on the material and observed the transition to a superhydrophobic-like state at long (15 min) etching. A few years later in 1993 Ogawa et al. [21] roughened glass surfaces in  $\text{CHF}_3/\text{O}_2$  plasmas and coated them with a perfluorinated monolayer to render glass superhydrophobic. In 1999 Youngblood et al. treated Poly(ethylene) (PE) and PTFE simultaneously in an Ar plasma, and observed roughening of PE and superhydrophobic behavior after 100 min of treatment [22]. Plasma deposition was also used as early as 1982 to deposit highly non-wettable films, such as PTFE [23], and in 2000 to deposit superhydrophobic fluorocarbon (PTFE-like) polymer in  $\text{CH}_4/\text{C}_4\text{F}_8$  plasmas [24]. These early efforts were reviewed in 2001 by Nakajima et al. [25].

Etching of organic crystalline polymers at relatively large pressures was shown to create roughness on their surface. The roughening step can be followed by a hydrophobic deposition layer either in the plasma or by other methods. This way Teshima et al. [26] produced superhydrophobic Poly(Ethylene terephthal-

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