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Assessing Omniphobicity by Immersion

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KEYWORDS: Omniphobicity; Contact angles; Immersion; Underwater; Wetting; Textured surfaces

Abstract**Hypothesis:**

Coating-free approaches to achieve liquid repellent, or omniphobic, surfaces could exploit inexpensive intrinsically wetting materials, such as polyethylene terephthalate and nylon, for applications such as liquid-vapor extraction and drag reduction. However, it is not clear whether the existing criteria for assessing coating-based omniphobicity, based on apparent contact angles, would be reliable for coating-free approaches, especially considering localized defects/damages during manufacturing and usage.

Experiments:

We assessed the omniphobicity of silica surfaces adorned with arrays of doubly reentrant pillars, cavities, and hybrid designs with sessile drops and on immersion in water and hexadecane through contact angle goniometry and confocal microscopy, respectively.

Findings:

We demonstrate that the assessment of omniphobicity of surfaces derived from intrinsically wetting materials can be misleading, if solely based on the measurement of contact angles. Specifically, localized defects in microtextures consisting of pillars may lead to the spontaneous loss of omniphobicity and detecting them through contact angles can be difficult. We also demonstrate that the immersion of those surfaces into probe liquids may serve as a simple and quick ‘litmus’ test for omniphobicity. Thus, immersion as additional criterion for omniphobicity might prove itself useful in the context of large-scale manufacturing.

1. Introduction

Omniphobic surfaces *repel* both polar and apolar liquids and are used in numerous applications that require immersion in liquids, such as the reduction of frictional drag [1, 2], biofouling, and scaling [3], and membrane-enhanced extraction of desalinated water [4-7] and alcohols [8]. A first subset of those surfaces, namely water-repellent surfaces, was produced in the early 20th century by exploiting hydrocarbon coatings [9-13]. However, it was not until the mid-nineties that Onda and co-workers reported on surfaces exhibiting super-repellence to both water and oils, with the synthesis of anodically oxidized alumina membranes coated with perfluorinated chemicals [14]. Simultaneously, the discovery of the lotus effect [15] inspired researchers worldwide to mimic natural systems such as beetles [16], spider webs [17], pitcher plants [18], sand dollars [19], and springtails [20], leading to the rational development of materials and devices for new applications [21]. Current liquid-repellent surfaces exploit chemical coatings and non-specific roughness. The criteria for quantifying the liquid-repellence of solid surfaces are based on measuring contact angles – advancing, θ_A , receding, θ_R , and (advancing) apparent, θ_f – of sessile droplets of water and apolar liquids (e.g. hexadecane) in air. Surfaces are categorized as ‘omniphobic’, if for both water and hexadecane, $\theta_f > 90^\circ$ [22, 23]; they are ‘superomniphobic’ if, for water and hexadecane, $\theta_f > 150^\circ$ and $\theta_A - \theta_R < 20^\circ$ [24] ‘hydrophobic’, if for water, $\theta_f > 90^\circ$ [12, 25]; and ‘superhydrophobic’, if for water, $\theta_f > 150^\circ$ and $\theta_A - \theta_R < 20^\circ$ [26]. Functionally, when coating-based omniphobic surfaces come into contact with liquids—sessile or pendant drops, or on immersion—the microtexture entraps air leading to Cassie states [11-13, 15, 27]. Those Cassie-states transition to the Wenzel state gradually through a variety of mechanisms, including capillary condensation and gas dissolution [19, 27-31]. Thus, contact angles present a reliable and simple criterion for assessing omniphobicity [12, 25, 26, 32-

34]. Researchers have also identified the limits at which coating-based superhydrophobicity spontaneously breaks down as a function of the solid-liquid (ϕ_{LS}) and liquid-vapor (ϕ_{LV}) area fractions of the microtextures [35, 36]; complementary scenarios entailing the variation of breakthrough pressures (P) [37] and surface tensions of water-alcohol mixtures [38] on fixed micropatterns have also been investigated. In those cases, Cassie-states transition to the Wenzel state instantaneously through liquid instabilities. However, outside that ‘critical’ parameter space (ϕ_{LS} , ϕ_{LV} , P), coating-based superomniphobicity is robust against localized defects, as confirmed by numerous reports [1-8, 11, 12, 22, 30, 39-51]. On the other hand, we are interested in the realization of coating-free omniphobicity that is robust against defects/damages that appear on real-world surfaces from manufacturing and use.

In the recent years, new approaches for achieving omniphobicity without completely relying on chemicals have been explored due to coatings’ environmental impact, cost, and vulnerability to high temperature and harsh cleaning procedures [52-56]. It has been demonstrated that by microtexturing mushroom-shaped pillars [24, 42, 57-61] (Figure 1A-C) and cavities [20, 23, 28, 62-65] (Figure 1D-F), even intrinsically wetting surfaces could entrap air and those metastable states could last for weeks or months. Indeed, those biomimetic approaches could potentially lead to coating-free solutions based on inexpensive materials. However, it is not entirely clear whether the criteria based on contact angles are adequate to assess the omniphobicity of those surfaces. Furthermore, while liquid repellent surfaces are typically characterized by high apparent contact angles, low contact angle hysteresis, and the entrapment of air on immersion in liquids (Cassie-states), the relative importance of those factors while assessing omniphobicity is not entirely clear. Herein, we clarify those issues by carefully investigating wetting of microtextured silica surfaces through two seemingly complementary

criteria: (i) contact angles of sessile drops, and (ii) immersion, with multiple probe liquids and experimental techniques. We demonstrate that for certain omniphobic microtextures localized surface defects could lead to catastrophic wetting transitions and detecting them through contact angles might be difficult/unreliable. In response, we propose immersion of surfaces in probe liquids as a reliable additional criterion for characterizing wetting.

2. Methods

2.1. Microfabrication

We created arrays of mushroom-shaped pillars (Figure 1A-C) and cavities (Figure 1D-F) onto silicon wafers (p-doped, 4" diameter and 500 μm thick with 2.4 μm thick thermally grown oxide layer). The wafers were cleaned in a piranha solution, $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 4:1$ by volume, maintained at $T = 388 \text{ K}$ for 10 min, followed by spin-drying under N_2 environment, and exposed to the vapor of hexamethyldisilazane (HMDS) to improve adhesion with the photoresist (AZ-5214E). A 1.6 μm thick layer of AZ-5214E, a positive photoresist, was spun-coat on them. The desired features were designed *in silico* through the Tanner EDA L-Edit software and transferred onto the wafers through photolithography in a Heidelberg Instruments direct-writing system (μPG501). After the UV exposure, the photoresist was removed using the AZ-726 developer. The exposed SiO_2 top layer was etched in an inductively-coupled plasma (ICP) reactive ion etcher (RIE) (Oxford Instruments - Chamber conditions: 10 mT, RF power: 100 W, ICP power: 1500 W, C_4F_8 flow: 40 sccm, and O_2 flow: 5 sccm, $T = 10 \text{ }^\circ\text{C}$, and $t = 16 \text{ min}$). A small indentation was created in the silicon layer through 5 cycles of anisotropic etching using the Bosch process, involving alternating depositions of C_4F_8 passivation layers (C_4F_8 gas

pressure, 30 mT; C_4F_8 flow 100 sccm; SF_6 flow: 5 sccm; RF power: 5 W; ICP at 1300 W; $T = 15$ °C for 5 s) and SF_6 gas for etching (pressure: 30 mT; RF power 30 W; ICP power: 1300 W; C_4F_8 flow: 5 sccm; SF_6 flow: 100 sccm; $T = 15$ °C for 7 s). This was followed by an isotropic etch (SF_6 flow: 110 sccm; 30 mT pressure; RF power 20 W; ICP power: 1800 W; $T = 15$ °C for 16 s). Next, a 500 nm thick thermal oxide layer was grown using a Tystar furnace. The top and bottom layers of the thermal oxide were subsequently etched, using the ICP-RIE described above. The wafers were then transferred to deep-ICP-RIE (Oxford Instruments) to etch the Si under the SiO_2 layer leading to the three different microtextures, namely (i) mushroom-shaped pillars or doubly reentrant pillars (DRPs), (ii) mushroom-shaped cavities or doubly reentrant cavities (DRCs), and (iii) hybrid structures consisting of DRPs surrounded by walls with doubly reentrant profile (Hybrids).

2.1.1. Mushroom-shaped cavities

5 cycles of anisotropic etching (described above) followed by piranha cleaning and isotropic etch (described above) for 125 s to create the void behind the added sidewall of the thermal oxide, which formed the mushroom-shaped edge of the cavity. The final step deepened the cavities up to $h \approx 60$ μm , using the same anisotropic recipe for 240 cycles.

2.1.2. Mushroom-shaped pillars and the hybrids

160 cycles of the anisotropic process followed by piranha cleaning and isotropic etch for 5 min to create the void behind the added sidewall of the thermal oxide, which formed the mushroom-shaped edge.

2.2. Characterization

After microfabrication, the samples were cleaned with fresh piranha solution (H_2SO_4 : $\text{H}_2\text{O}_2 = 4:1$ by volume at $T = 388$ K) for 10 min, blow-dried with a 99% pure N_2 pressure gun, and stored in glass petri dishes in a vacuum oven (Lindberg) at $T = 323$ K for 48 h. Subsequently, the apparent advancing/receding contact angles with deionized water and hexadecane were measured using a Kruss Drop Shape Analyzer DSA100 at $0.2 \mu\text{L}\cdot\text{s}^{-1}$ at multiple locations on each sample. All the data were analyzed using the *Advance* software. We recorded liquid drops impacting the surfaces with a Phantom v1212 high-speed camera from Vision Research. A Zeiss LSM710 upright confocal microscope enabled the investigation of time-dependent wetting transitions on immersion in water and hexadecane using Rhodamine B and Nile Red respectively. All the samples were coated with a 4 nm Au/Pd layer prior to scanning electron microscopy (Nova Nano).

3. Experimental Results and Discussion

To elucidate the importance of immersion as the additional crucial criterion, we assessed the omniphobicity of silica surfaces with arrays of mushroom-shaped pillars and cavities (Figure 1, Methods). Henceforth, we refer to those pillars and cavities as doubly reentrant pillars (DRPs) and doubly reentrant cavities (DRCs), respectively. The arrays of DRPs and DRCs were designed such that the normalized area of contact at the liquid-solid, ϕ_{LS} , and liquid-vapor, ϕ_{LV} , interfaces, under sessile drops, were similar (Section S1; DRPs: $\phi_{\text{LS}} = 0.04$, $\phi_{\text{LV}} = 0.96$; DRCs: $\phi_{\text{LS}} = 0.24$, $\phi_{\text{LV}} = 0.80$). Next, following the standard criteria for assessing the omniphobicity of surfaces, we measured the advancing, receding, and apparent contact angles of droplets of water (intrinsic contact angle on flat and smooth SiO_2 in air, $\theta_o = 40^\circ$) and hexadecane ($\theta_o = 20^\circ$), dispensed/retracted at $0.2 \mu\text{L/s}$ (Methods, Table S1). We found that:

1. SiO₂ surfaces with arrays of DRPs **exhibited superomniphobicity** for both liquids; the apparent contact angles, $\theta_t > 150^\circ$ and the contact angle hysteresis was minimal; liquid droplets bounced off the surfaces when dropped from a height of $h \approx 4$ mm (Table 1, Movie S1-2).
2. SiO₂ surfaces with arrays of DRCs **exhibited omniphobicity** in air, with apparent contact angles, $\theta_t > 120^\circ$ for both liquids (Table 1). The receding contact angles, θ_R , were found to be $\approx 0^\circ$ because of the lack of discontinuity of the solid-liquid interface, such that the receding liquid meniscus was not required to locally detach from the solid, similarly to what was observed with pillars [66-69].

Thus, based on contact angles alone, one would conclude that SiO₂ surfaces with arrays of DRPs and DRCs were both omniphobic (Table 1, Figures 2A and 2E).

Figure 1. Scanning electron micrographs of (A-C) doubly reentrant pillars (DRPs) and (D-F) doubly reentrant cavities (DRCs). D , L , l represent the diameter, pitch, and the height of the doubly reentrant feature of the DRCs and DRPs respectively.

Our next step was to investigate the behavior of those surfaces on immersion. Although there is no clear definition of omniphobicity on immersion, it is reasonable to expect surfaces designated as ‘omniphobic’ and ‘superomniphobic’ to trap air in the microtexture and sustain it under our experimental conditions (293 K, 1 atm, and 60% relative humidity). Immersion entails liquid contacting the (i) microtexture boundary, and (ii) the defect sites. In the case of DRP arrays, localized defects, such as missing/broken pillars, exposed the ‘stems’ of the pillars to liquids, which was also the case at the boundary. Thus, microtexture boundary acted as a surrogate for local defects. While defect-free DRP arrays exhibited superomniphobicity in air,

liquid drops advancing from the boundary penetrated inside the microtexture leading to spontaneous loss of omniphobicity (Figures 2A-D, Movie S3). In contrast, for DRC arrays, liquid drops advancing from the boundary were repelled from the microtexture and drops on the microtexture maintained Cassie-states due to their compartmentalized nature (Figures 2E-H). Our next experimental protocol for immersion involved placing the samples in clean glass petri dishes and introducing probe liquids (water and hexadecane) at the rate of 2 mL/min, leading to $z \approx 5$ mm thick columns, and recording their response (Methods). Against our expectation, silica surfaces with arrays of DRPs, which we assumed would be superomniphobic, based on contact angle measurements in air, got filled by both liquids instantaneously ($t < 1$ s) - they exhibited 'omniphilicity'. On the other hand, silica surfaces with arrays of DRCs entrapped air on immersion, in both liquids (Figures S1, Table 1). To visualize the air inside the DRCs immersed in liquids at a higher spatial resolution, we used a confocal microscope (Methods). Indeed, DRCs reliably trapped air on immersion for both water and hexadecane - Figures 2I-J present the isometric reconstructions of the liquid-vapor interfaces in those experiments. Thus, cavity-based architectures with reentrant or doubly reentrant profiles are deemed omniphobic from either assessment criterion.

Figure 2. Behaviors of wetting liquids at the edge of the microtextures consisting of DRPs and DRCs both microfabricated on silica surfaces. (A-D) The superomniphobicity of microtextures consisting of DRPs depends on preventing exposure to their boundaries (also surrogates for localized defects); wetting liquids imbibe inward from the boundary, and the superomniphobicity is lost instantaneously. (E-H) In contrast, microtextures consisting of DRCs do not suffer from this vulnerability. (I-J) Computer-enhanced 3D reconstructions (Center) of liquid-vapor interfaces **after 5 min of immersion** of silica surfaces with circular DRCs under $z \approx 5$ mm thick column of water (blue) and hexadecane (yellow), confirming the entrapment of air. Cross-sectional views of the 3D reconstruction along the black dotted lines) are shown on either sides. White arrows and marks indicate the locations of the doubly reentrant features, where the liquid menisci gets stabilized. (Scale bar: diameter of DRCs, $D = 200 \mu\text{m}$)

Considering the immersion of surfaces in liquids as an additional criterion for assessing omniphobicity, we modified our silica surfaces with arrays of DRPs to achieve omniphobicity on immersion. We microfabricated walls with doubly reentrant features around DRPs to insulate their stems from the wetting liquids (Figure 3A-C). This strategy proved itself to be effective - the hybrid microtextures entrapped air on immersion (Figure 3D-E, S2-3 and Movie S4, Table 1). Thus, silica surfaces with hybrid microtextures exhibited omniphobicity on immersion by trapping air.

Figure 3. (A-C) Scanning electron micrographs of our hybrid design consisting of arrays of DRPs surrounded by doubly reentrant walls to overcome their vulnerability at the boundaries. (D-E) Computer-enhanced 3D reconstructions of representative confocal images (isometric and cross-sections along the dotted lines) of wetting transitions in silica surfaces with doubly reentrant pillars immersed under a $z \approx 5$ mm column after 5 minutes of immersion of (D) water, and (E) hexadecane. The (false) blue and yellow colors correspond to the interfaces of water and hexadecane with the trapped air. Intruding liquid menisci were stabilized at doubly reentrant rims of the pillars and the side wall. (Scale bar: Pitch, pillar-to-pillar center distance is 100 μm)

An assessment of the omniphobicity of all the surfaces investigated in this work, based on the contact angle measurements and the entrapment of air on immersion, is presented in Table 1.

Table 1. Criteria for assessing the omniphobicity of surfaces based on contact angle measurements –advancing (θ_A), receding (θ_R), and apparent (θ_r)—and immersion in liquids.

Surfaces	Criterion: Contact angles in air			Criterion: Immersion	
		Water	Hexadecane	Water	Hexadecane
DRPs	θ_{r}	$153^{\circ}\pm 1^{\circ}$	$153^{\circ}\pm 1^{\circ}$	Instantaneous penetration	Instantaneous penetration
	θ_{A}	$161^{\circ}\pm 2^{\circ}$	$159^{\circ}\pm 1^{\circ}$		
	θ_{R}	$139^{\circ}\pm 1^{\circ}$	$132^{\circ}\pm 1^{\circ}$		
Assessment:	Superomniphobic			Not omniphobic – in fact, <i>omniphilic</i>	
DRCs	θ_{r}	$124^{\circ}\pm 2^{\circ}$	$115^{\circ}\pm 3^{\circ}$	Trapped air (omniphobic)	Trapped air (omniphobic)
	θ_{A}	$139^{\circ}\pm 3^{\circ}$	$134^{\circ}\pm 5^{\circ}$		
	θ_{R}	0°	0°		
Assessment:	Omniphobic			Omniphobic	
Hybrids	θ_{r}	$153^{\circ}\pm 2^{\circ}$	$153^{\circ}\pm 2^{\circ}$	Trapped air (omniphobic)	Trapped air (omniphobic)
	θ_{A}	$161^{\circ}\pm 2^{\circ}$	$159^{\circ}\pm 2^{\circ}$		
	θ_{R}	0°	0°		
Assessment:	Omniphobic			Omniphobic	

Below we explain the mechanisms underlying the contrasting behaviors of silica surfaces with DRPs and DRCs on immersion. It has been demonstrated that doubly reentrant features, pillars or cavities, can stabilize sessile drops due to their geometry, such that if the drops were pushed into the microtexture the curvature at the solid-liquid-vapor interface resisted penetration (Figure 4 inset) [20, 24, 27, 28]. In fact, the concave curvature of the liquid meniscus gave rise to capillary pressure, also known as the ‘Laplace pressure’, that prevented the imbibition and has the following general expression $P_L = 2\gamma_{LV} \times \cos \theta_o \times C_m$, where γ_{LV} is the surface tension of the liquid, θ_o is the intrinsic contact angle at the solid-liquid-vapor interface at thermodynamic

equilibrium, and $C_m = 0.5 \times (1/R_1 + 1/R_2)$ is the mean curvature of liquid-vapor interface, and R_1 , R_2 the two mutually orthogonal radii of curvatures of the liquid-vapor interface [33]. Thus, the thermodynamically stable fully-filled (Wenzel) state could be delayed [27] (Figures 4 inset and upper-right corner, Figures 2 I-J, 3D-E). However, in the case of DRPs we found that boundaries, as surrogates for localized defects, enabled the contact between the liquid and the non-reentrant parts of the microtexture. On touching the stems of the pillars the curvature of the liquid reverted to convex and it imbibed instantaneously displacing the trapped air (Figure 4 bottom-right corner and Movie S3). For pillars, in this scenario, there were no kinetic barriers preventing the wetting transition to the thermodynamically stable fully-filled (or Wenzel) state [27] (Figure 2A and Movie S3). In contrast, for arrays of DRCs, the effect of localized damage did not propagate throughout due to the compartmentalized entrapment of air. Subsequently, the rate of loss of the trapped air depended on a variety of factors and mechanisms; a detailed report on those factors have appeared shortly [29]. Thus, immersion could help identify the vulnerability of the microtextured surfaces to localized defects that contact angles might not be able to detect easily.

Immersion tests might also prove useful for assessing the omniphobicity coating-based surfaces. For instance, in scenarios where coating-based (superhydrophobic) microtextures comprising pillars get contaminated along the stems of the pillars due to the adsorption of organic foulants, a common issue in desalination [35, 36, 56, 70]. While such a surface might be unfit for applications requiring immersion, assessments through contact angles might still indicate the surface to be superhydrophobic (Figure 4 – compare wetting behaviors at bottom left and right).

Figure 4. Schematic representation of our study showing the surface of an intrinsically wetting material adorned with doubly reentrant pillars (DRPs) exhibiting superomniphobicity, when assessed through measuring apparent contact angles in air (bottom left corner, where liquid drops sit like marbles). The same liquid, however, infiltrates the microtexture from the boundary, a surrogate for localized defects (right corner). Thus, immersing the surface identifies effects of localized defects that contact angles might miss. To enable DRP microtextures to entrap air on immersion, we microfabricated walls around them. The resulting microtextures trapped air on immersion in wetting liquids and the apparent contact angles of drops of water and hexadecane, $\theta_r > 90^\circ$. Those hybrid microtextures can be used for applications requiring immersion in wetting liquids.

4. Conclusion

The term ‘omniphobicity’ is context-dependent, just like the term ‘hydrophobicity’, meaning that the results of assessments can vary dramatically based on criteria such as immersion, applications, and time-dependent effects [19, 71]. While the coating-based

omniphobic surfaces lead to robust Cassie-states even in the presence of localized defects [1-8, 11, 12, 22, 30, 39-48], it has been demonstrated that the omniphobicity of surfaces derived from intrinsically wetting materials could be catastrophically lost due to localized defects [28]. Thus, in order to develop coating-free omniphobic surfaces, the effects of defects must be carefully assessed. In this work, we assessed the omniphobicity of coating-free silica surfaces with arrays of DRPs and DRCs through apparent contact angles and the entrapment of air on immersion in liquids (Cassie-states). Based on the contact angle measurements with sessile drops in air, we found that DRPs exhibited superomniphobicity. However, on immersion, those surfaces spontaneously imbibed the liquids. The imbibition was driven from the boundary of the microtexture, which was also representative of localized structural defects and damage - a common feature of real-world surfaces. In contrast, silica surfaces with arrays of DRCs and hybrid structures consisting of DRPs bound by doubly reentrant walls exhibited omniphobicity consistently, both with liquid droplets in air and on immersion. Interestingly, while the contact angle hysteresis of the probe liquids on silica surfaces with DRCs and hybrid DRPs was much higher than that for DRPs, their robustness at maintaining Cassie-states was superior to the latter (Table 1). Thus, the impact of low receding contact angles on liquid imbibition on immersion, an ‘advancing’ process, might not be significant and the stability of the entrapped air might be a relatively more important criterion. We do note though that contact angle hysteresis would matter while developing strategies for the regeneration of the trapped air by external stimuli [41, 72-74]. In summary, we have demonstrated that the assessment of omniphobicity by contact angles alone might miss the effects of localized defects due to structural and/or chemical heterogeneities, simply because it is performed on a limited number of spots. Therefore, immersion tests, which assess the entire surface, would be a valuable addition to contact angle

measurements towards assessing omniphobicity of coating-free microtextured surfaces. These insights also might be relevant to the context of mass production and structural health monitoring of omniphobic surfaces.

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Graphical Abstract