STUDY OF WETTABILITY FEATURES OF NATURAL SUPERHYDROPHOBIC SURFACES, BIOMIMICKING ASPECT, AND ELECTROWETTING ON DIELECTRIC SURFACES

A thesis submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

by

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DECEMBER 2024

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Conclusion and future prospects

In this chapter, we have summarized the main outcomes of our phenomenological studies and outlined the potential scope and future direction of research.

7.1 Conclusions

Chapter 1 provides a brief history and an overview of key concepts related to liquid droplet wettability, rolling, and bouncing on solid surfaces including theoretical support. **Chapter 2** delves into the basic mathematical background of droplet wetting dynamics, including the impact of surface roughness through the modified Wenzel and Cassie equations, as well as electrowetting phenomena. Here, we present a brief overview of the key conclusions derived from the four subsequent chapters:

- **Chapter 3:** Isotropic superhydrophobicity and adhesion features have been studied experimentally and a model support. The exceptionally high hydrophobicity observed in the tender, mature, and senescent abaxial leaf surfaces of *Ziziphus mauritiana*, which is attributed to their hairy, matted surface constructs. These leaves, with fibrous, textured surfaces, exhibit superhydrophobic properties, with water contact angles (WCAs) reaching up to $\sim 151.1°$. In contrast, the green adaxial surfaces are hydrophilic, with water contact angles ranging from approximately $\sim 66.4°$ to $75.9°$. Inspired by the abaxial leaf surface of *Ziziphus*, the electrospinning method was utilized to replicate this structure and create superhydrophobic PVDF (Polyvinylidene fluoride) polymer matted surfaces. These surfaces consist of microfibers with an average diameter of about $\sim 4.3\ \mu$m. The focus of the study was to explore the unique wetting properties of natural hairy, nonwoven fiber textures and to replicate them, linking surface texture to wettability characteristics. The electrospun PVDF microfibers demonstrated excellent superhydrophobicity and superadhesion, with water contact angles (WCA) of $\sim 145.7°$ and contact angle hysteresis (CAH) of $\sim 49.4°$. Furthermore, to understand the structural patterns of nonwoven matted microfibers, an analogy with the worm-like chain (WLC) model has been employed. This model explains the growth and spread of the fiber structure, highlighting its similarity to a yarn-like formation.

- **Chapter 4:** In this chapter, the remarkable anisotropic superhydrophobicity and unidirectional droplet rolling aspects are presented. The sword-lily (*Gladiolus hortulanus*) leaf, which exhibits a three-level surface structure possess anisotropic superhydrophobicity. The first level consists of micro-scale striations and protrusions (papillae), while the second level features nano-scale waxy flakes. The root mean square (rms) roughness of the leaf's surface shows a directional variation, with values of approximately $\sim$ 1.5–2.0 μm along the striated direction and $\sim$ 15.1–16.6μm perpendicular to it, indicating that wetting behaviour differs in these directions. Static contact angles (WCAs) are measured in the range of $\sim$ 143°–147° in the parallel (striated) direction and $\sim$ 156°169° in the perpendicular direction for droplets of varying sizes ($\sim$ 4-10 μL). The corresponding roll-off angles (α) for these droplet sizes are found to be $\sim$ 8°–23° along the parallel direction and $\sim$ 16°–41° along the perpendicular direction. Drawing inspiration from the natural water-repellent properties of the sword-lily leaf, a biomimicked polystyrene (PS) leaf surface is created using a soft lithographic method. The bio-mimicked PS replica shows static WCAs of $\sim$ 130°–139° along the parallel direction and $\sim$ 142°–145° along the perpendicular direction, with roll-off angles ranging from $\sim$ 21°–49° and $\sim$ 40°–55° in the respective directions. Both the natural leaf surface and the biomimicked PS surface are carefully examined, with a focus on their microstructure and roll-off behaviours. The relevant theoretical treatment is also highlighted.

- **Chapter 5:** This chapter investigates the interplay between surface adhesion, structure, and (super)hydrophobicity on low- and high adhesion surfaces, and their influence on droplet contact time and maximum spreading during impact. For the first time, we report the droplet impact dynamics on the superhydrophobic abaxial leaves of Indian jujube (*Ziziphus mauritiana*) and *Kalanchoe fedtschenkoi*. Additionally, two hydrophobic abaxial leaf surfaces with high adhesion, *Mesua ferrea* and *Litchi chinensis* (*Litchi*), were studied. The micro- to nano-scale surface morphology of these leaves is crucial in determining both static and dynamic wettability. Droplets impacting the *Kalanchoe* leaf surface, with Weber numbers (We) $\sim$ 2.8, 14.4, and 25.8, exhibited complete rebound. This behavior is attributed to the low-adhesion, nanostructured surface (WCA $\sim$ 156°, CAH $\sim$ 5°). In contrast, the *Ziziphus* abaxial leaf surface (WCA $\sim$ 151°, CAH $\sim$ 30°) showed a partial rebound state. The *Ziziphus* leaf's abaxial structure, characterized by an irregular, yarn-like, micro-fibrous matted pattern with high adhesion, led to a collapsed region upon droplet impact. This resulted in a transition from the Cassie to the Wenzel state during the impact. The hydrophobic leaves *Mesua* (WCA $\sim$ 146°, CAH $\sim$ 39°) and *Litchi* (WCA $\sim$ 130°, CAH $\sim$ 32°) also demonstrated complete droplet rebound. The droplet impacts (We

~ 25.8) on these low- and high-adhesion inclined surfaces revealed that increasing the surface tilting angle (T.A.) from ~ 0° to 30° significantly reduced contact time. This reduction arises from rapid detachment caused by asymmetric spreading and retraction, where the differing tangential velocity components in the x- and y-directions on inclined planes play a key role.

- **Chapter 6:** In this chapter, two aspects of electrowetting phenomena have been investigated: (i) a planar liquid lens experiment and (ii) a numerical simulation of an adaptive liquid lens using COMSOL Multiphysics® software. For the planar liquid lens, we used two oil media—Johnson's® mineral oil and silicone oil—as insulating liquids, with a KCl saltwater droplet as the conducting liquid. As the applied voltage increases, the contact angle (CA) of the saltwater droplet decreases up to a certain point, after which it stabilizes, reaching a contact angle saturation (CAS). This change in CA alters the oil-saltwater droplet interface curvature, which in turn modifies the focal length. The observed focal length varied from ~14.92 mm to ~15.78 mm for silicone oil and from ~8.85 mm to ~9.37 mm for Johnson's® mineral oil in the voltage range of ~0-120 V.

In addition to the planar liquid lens, a simulation study was conducted on an adaptive liquid lens based on the electrowetting on dielectric (EWOD) principle. The model involved three insulating liquids—silicone oil, *n*-hexadecane, and ®-tetradecane, inside a cylindrical chamber with two different hydrophobic dielectric surfaces: Parylene-C and Teflon-AF. The simulation showed that applying a bias voltage above approximately 90 V modulates the interfacial layer between the immiscible liquids, switching the lens curvature from diverging to converging one. The focal length ranged approximately ±400 mm for both hydrophobic surfaces across the 0-120 V voltage range. However, near the curvature switching point, the focal length indicating a discontinuity at this transition. The study also explored the effects of applied voltage and dielectric layer thickness on curvature transition and focal lengths, providing insights into the practical challenges for developing industrial-grade liquid lenses.

7.2 Applications

Inspired by natural surfaces, researchers are actively engaged in developing multifunctional, self-sustaining superhydrophobic materials. These robust biomimetic surfaces are in high demand across various fields due to their unique water-repellent properties. Applications range from self-cleaning coatings and solar energy harvesting to water collection, oil–water separation, water purification, and integration into smart devices, as discussed below.

Solar energy: Solar energy is a widely used and abundant renewable source. However, in sunny regions, dust and particulate matter often accumulate on solar panels, blocking sunlight and raising cell temperatures, which lowers photovoltaic efficiency. Applying a self-cleaning superhydrophobic coating can help maintain panel performance by preventing dust buildup [260].

Water collection: The key feature of a nature-inspired surface, such as that of the desert beetle, lies in its ability to efficiently condense water vapor and consistently release the collected droplets [261]. Biomimetic collectors, inspired by nature, often use a superhydrophobic background to repel water and hydrophilic tips to capture and guide droplets, improving water collection [261].

Water –oil separation: To enable biomimetic application in oil–water separation, the sponges were modified with low-surface-energy materials and engineered to have nano- and microscale hierarchical roughness [262]. These structural and chemical modifications significantly altered the surface wettability of the sponges, rendering them superhydrophobic and superoleophilic. As a result, the sponges can effectively repel water while selectively absorbing oil. This dual wettability behavior facilitates efficient oil–water separation and industrial wastewater treatment applications.

Programmable droplets system: A programmable droplet system based on electrowetting requires a superhydrophobic coating on the chip surface. It employs an insulating, superhydrophobic substrate that ensures protein or cell droplets do not leave any residue as they move across the surface [263]. This feature allows for the manipulation of a variety of biological materials on a single platform without the risk of cross-contamination.

7.3 Limitations

Many researchers have drawn inspiration from nature to create superhydrophobic surfaces, which typically exhibit very high static contact angles and distinct adhesion properties, such as those seen on lotus leaves (low adhesion) and rose petals (high adhesion). Building on this natural inspiration, this thesis explores the surface texture, dynamic wettability, and biomimetic characteristics of specific plant leaf surfaces. However, bioinspired superhydrophobic surfaces, while highly effective in certain contexts, face several significant limitations:

1. **Replicating hierarchical structures**: Natural superhydrophobic surfaces exhibit structural variations ranging from single-scale to multiscale topographies. Many leaves display a hierarchical architecture with both micro- and nanoscale roughness, and replicating such complex structures with precise control at multiple scales remains a significant experimental challenge. The surface morphology of the *Ziziphus* leaf is particularly intricate due to its irregular fiber distribution, despite featuring a single-level microfiber texture. To achieve a

comparable biomimetic surface, careful selection of the fabrication technique and a thorough optimization process are quite essential. Electrospinning was selected taking advantage of its suitability for replicating microfibers in nonwoven form. However, matching the fiber diameter and distribution feature with that of the natural leaf surface was done through several trials and optimization of the key parameters (see Appendix I). In contrast, the sword lily leaf exhibits a more complex structure with three distinct levels of surface texture. The replication of such a surface offered challenges as regards the selection of a suitable replication technique as well as the choice of hydrophobic polymer material. Soft lithography was chosen for its accessibility and ability to reproduce multilevel textures with case. Despite this, optimizing the soft lithography process to replicate the native surface as is remained challenging (see Appendix II), and nanoscale features were still not fully captured. Although efforts were made to mimic the structural morphology, further research is needed to evaluate the durability, environmental stability, mechanical robustness, and other performance parameters of the fabricated surfaces.

2. **Surface chemistry and materials**: In the biomimetic process, hydrophobic materials are typically used to enhance surface water-repellency through micro- and nano-scale texturing. Polymers such as polydimethylsiloxane (PDMS), polyvinylidene fluoride (PVDF), and polystyrene (PS) are commonly employed due to their compatibility with existing fabrication techniques. However, these polymers are non-biodegradable and not environmentally friendly. This limitation can be addressed by exploring biodegradable hydrophobic materials, although they often require novel and more complex fabrication strategies.

3. **Durability and longevity of biomimetic surfaces**: Leaves such as lotus, taro, and rose display superhydrophobicity through hierarchical surface textures and wax coatings. Over time, biological growth leads to surface texture evolution, while environmental factors like UV exposure, dusts, and mechanical abrasion degrade the wax layer. Aging also alters the integrity of micro/nanostructures, and surface contamination or microbial growth can disrupt air retention capability. As a result, the superhydrophobic effect diminishes gradually with age and time [264]. Despite significant advancements in the fabrication of biomimetic superhydrophobic surfaces, durability and longevity remain major obstacles to their practical application [24]. The delicate micro and nanoscale structures, essential for maintaining air gaps and achieving extreme water repellency, are highly susceptible to mechanical wear, chemical degradation, and environmental factors such as high humidity, impact forces, and thermal stresses. Surface flooding, droplet pinning at defects, and loss of air

pockets under elevated pressures severely compromise performance over time. Moreover, many current fabrication techniques do not inherently strengthen the structural robustness or self-healing capabilities needed for long-term use [24]. Without reinforcing both the mechanical integrity and chemical stability of these textured surfaces, the superhydrophobicity quickly degrades, limiting their lifespan. Therefore, enhancing the intrinsic properties through strategies like hierarchical structuring, flexible substrates, protective coatings, or self-replenishing chemistries is crucial to achieving resilient, long-lasting biomimetic surfaces suitable for widespread industrial deployment [265]. We have fabricated biomimetic surfaces using various polymer materials such as PVDF, PS, and PVA, and have extensively studied their wetting characteristics. However, to advance the practical applicability of these surfaces, it would be highly valuable to investigate their durability and longevity under mechanical, chemical, and environmental stresses. Future research focusing on systematic durability testing could provide critical insights into maintaining superhydrophobic performance.

4. **Scalability**: Replicating nature-inspired structures on a large scale can be challenging and costly, as it often requires highly expensive advance micro- and nano-fabrication techniques.
5. **Contamination Sensitivity**: Superhydrophobic surfaces can lose their water repellency if contaminated by oils or dust particles smaller than the texture pore size, reducing their effectiveness in practical applications.
6. **Dynamic Performance**: Although some surfaces perform well in static conditions, their water repellency may decrease under dynamic conditions (e.g., water impact or flow) due to drag forces.
7. **Material Constraints**: Maintaining superhydrophobicity is challenging with certain materials, restricting applications to substrates that can support or maintain this property.

7.4 Future prospects

This thesis has explored isotropic and anisotropic wetting, biomimicry, and electrowetting. The electrowetting technique allows for precise control over droplet directionality and the ability to transition droplets from non-wetting ($>90^\circ$) to superwetting ($<10^\circ$) states on artificial superhydrophobic surfaces. Several key research areas offer promising opportunities for future industrial applications and technological advancements:

- Drawing inspiration from natural surfaces, the development of smart artificial surfaces that exhibit both superhydrophobicity and superoleophobicity could be a significant area of progress.

- In addition to super adhesion, the ability to transition between superhydrophobic and superhydrophilic states holds substantial potential, especially in microfluidics and soft matter physics.

- Future applications include optomechanics, microfluidics, medical care, and “cool roof ”properties through control of microfiber diameter and density.

- Investigating droplet dynamics on charged surfaces, liquid-infused surfaces, and soft/elastic surfaces could lead to specialized applications.

- The exploration of low-voltage electrowetting, CA saturation on biomimicked superhydrophobic surfaces remains a largely unexplored avenue, presenting significant research potential.

- Building on simulations of adaptive liquid lenses, a prototype of a tunable liquid microlens could be developed, supported by relevant programming advancements.