Chemical Approaches for Reliable Superhydrophobic Coatings: Synthesis and Applications

A THESIS

submitted by

Avijit Baidya

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Chemical Approaches for Reliable Superhydrophobic Coatings: Synthesis and Applications

Avijit Baidya

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Abstract

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Abstract

Biologically available surfaces having unique liquid repelling properties have become some of the most intensely pursued materials in the past few years. In this context, several living creatures have already been studied in great detail. Surface roughness (nano/microscale) and chemical functionalities being the underlying reason for such phenomena, artificially designed these surfaces have already proven their application potential in different fields of science and technology, directed to solving many global challenges. Although various methods have been proposed for the development of these bio-mimicked surfaces, most of the time, complex multi-step processes, affordability of initial materials, large-scale production, and durability restrict the use of these in day-to-day life. Again, use of organic solvents pose concerns related to safety, environmental pollution, operational cost, storage and transport. From an industrial point of view, these limit the commercialization of these materials and their bulk production.

In view of the current scenario, our work mostly focused on the development of coating materials through green and industrially adaptable or feasible ways that provide durable liquid repelling films over diverse array of substrates. Water being an economic and environmentally accepted solvent system, fabrication of these materials was carried out solely in water at room temperature. With regard to primary ingredients, use of affordable materials like clay and cellulose enhanced the possibility of scale up. Along with the mechanical and chemical durability of the coated surfaces, application domains of these materials were identified and demonstrated.

In the introduction (Chapter 1), evolution of the concept of "bio-mimicry" followed by its influence on the development of liquid repelling surfaces are discussed. Objectives and motivations of the work are presented in Chapter 2. Chapter 3 covers the details of ingredients, synthesis, experiments and fabrication of the working prototypes.

Chapter 4 (publication I) & 5 (publication II) focus on the fabrication of waterborne superhydrophobic coating materials from cellulose nanofiber and clay. Fabrication of durable multi-functional waterproof paper was demonstrated for both cases, needed for various upcoming technologies including microfluidics and various paper-based technologies. In addition, publication II showed the under oil superhydrophobic property of the coated material. Chapter 6 (publication III) reports the fabrication of transparent solid slippery surface and its use in atmospheric water capture through a working prototype.

Chapter 7 summarizes the above-mentioned results and gives a future perspective on this research area.

We believe that the methodologies and materials presented here can be successfully implemented to various technologies or translated to useful products or devices that will be helpful for human civilization.

Keywords superhydrophobicity, robust, solid slippery, liquid repellency

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Dedicated to my parents

THESIS CERTIFICATE

This is to certify that the thesis entitled **CHEMICAL APPROACHES FOR RELIABLE SUPERHYDROPHOBIC COATINGS: SYNTHESIS AND APPLICATIONS,** submitted by **Avijit Baidya** to the Indian Institute of Technology Madras, India and Aalto University, Finland for the award of the joint degree of **Doctor of Philosophy and Doctor of Science (Technology)** is a bonafide record of research work carried out by him under our supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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Research Guides

✓

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Preface

The research presented in this thesis has been carried out at Indian Institute of Technology, Madras, Department of Chemistry, and Department of Mechanical Engineering with the collaboration of Department of Applied Physics at Aalto University during the years 2013 to 2018. It was a great pleasure to work with different people from different continents and adopting their lifestyles and cultures in various course of the timeline. These five years have been extremely impactful, valuable and efficient in time management. At the same time, it was so enjoyable and meaningful. Thanks to the awesome people around with whom I got a chance to collaborate and discuss scientific ideas. To me, research is like a puzzle and full of mysteries. It exhausts the mind and drains energy. It squeezes life and soul with stress, tension and frustration to deliver the best out of you. However, the best thing about it is that at the end of this long journey, you became a person to think, design and deliver according to the need of the society. You earn respect. In the course of time, you learn to be a responsible and trustworthy person. It changes your vision. Every single day you get up, becomes the day with new thoughts, new challenges, and new possibilities. It teaches the importance of time and the power of working as a team. In each and every step you enrich yourself and every individual around you with knowledge. At this stage, certainly, I can feel the changes happened within myself including the development of attitude, skills, thinking style and many others. I can see a new version of Avijit Baidya with full of confidence and depth of experience.

My journey towards the completion of this thesis has been truly wonderful. First of all, I would like to thank my parents, sister and brother who supported me throughout my life. Their constant love and care have been invaluable in my life.

I consider myself heartily thankful to my advisors **Prof. T. Pradeep, Prof. Robin Ras and Prof. Sarit K. Das** for making this journey worthwhile. I am extremely fortunate to have them as my advisors, who gave me the freedom to explore on my own, and at the same time monitored my progress with extreme patience. Their constructive criticism showed me the right way when I made mistakes.

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I express my sincere thanks to my doctoral committee members; Prof. Sundargopal Ghosh (CY), Prof. G. Ranga Rao. (CY) and Prof. Vijayan C (PH) for giving their valuable time and showing interest in my work. Their support and criticisms have helped to give a new direction in the work. I extend my thanks to the Dean, Academic Research for the development of cordial research atmosphere in the campus. I thank the former Heads of the Department of Chemistry; Prof. U. V. Varadaraju, and the present Head, Prof. Indrapal Singh Aidhen, for proving the world-class facilities related to the scientific research. I also thank different funding agencies without whose support this work could not be done. I would like to thank the Department of Science and Technology (DST), Government of India for constantly supporting our research program. I would also like to express my gratitude towards the DST INSPIRE, Government of India from whom I have received my research fellowship. I would like to thank Finnish National Agency for Education for making double/joint degree possible with Aalto University. I would like to express my sincere thanks to all the staff members of the Department of Chemistry for their timely help and support throughout my research work.

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During my research life in IITM, I had opportunity to work with several people from different backgrounds. I would like to express my deep gratitude for helping me in different stages and making my research truly interdisciplinary. I would like to thanks all the lab members from HTTP lab, Mechanical engineering, IIT Madras. It was my pleasure to get opportunity to discuss science with Prof. Mahesh V Panchagnula and his lab members. I would like to thank Prof. Pijush Ghosh and Prof. Abhijit Deshpande for giving their valuable time in scientific discussions. I would like to thank Arjun, Pratik, Ramya for helping me in scientific studies.

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I would like to acknowledge all those people whom I have met in the hostel and various departments. I would like to express my gratitude to all my friends for their unconditional friendship and making my days memorable. I am very lucky to have wonderful juniors. Their constant love and close friendships have made my stay in this campus meaningful and relaxed even in tremendous pressure.

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AVIJIT BAIDYA

Chennai

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List of Publications

List of Papers Based on This Thesis

I. Organic solvent-free fabrication of durable and multifunctional superhydrophobic paper from waterborne fluorinated cellulose nanofiber building blocks. **Avijit Baidya**, Mohd Azhardin Ganayee, Swathy Jakka Ravindran, Kam (Michael) Chiu Tam, Sarit Kumar Das, Robin H. A. Ras, Thalappil Pradeep, ACS Nano (2017), 11(11), 11091-11099.

II. Fabrication of a waterborne durable superhydrophobic material functioning in air and under oil. **Avijit Baidya**, Sarit Kumar Das, Thalappil Pradeep, Advanced Materials Interfaces, (2018), DOI: 10.1002/admi.201701523.

III. An aqueous composition for lubricant free, robust, slippery, transparent coatings on diverse substrates. **Avijit Baidya**, Sarit Kumar Das, Thalappil Pradeep, Global Challenges (2018), 2, 170097.

Author’s Contribution

Publication I: Organic solvent-free fabrication of durable and multifunctional superhydrophobic paper from waterborne fluorinated cellulose nanofiber building blocks.

The author had the main responsibility for building the idea through the understanding of chemical nature of material, designing and performing the experimental work, interpretation of the results and writing the manuscript. Mohd Azhardin Ganayee conducted the AFM measurements. Swathy Jakka Ravindran conducted the anti-microbial study.

Publication II: Fabrication of a waterborne durable superhydrophobic material functioning in air and under oil.

The author had the responsibility for building the idea, designing and performing the experimental work, interpretation of the results and writing the manuscript. Some of the experiments (AFM and antimicrobial study) were performed with help of lab mates in order to defend reviewers’ comments.

Publication III: An aqueous composition for lubricant free, robust, slippery, transparent coatings on diverse substrates.

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Other Publications

IV. Diffusion-controlled simultaneous sensing and scavenging of heavy metal ions in water using atomically precise cluster-cellulose nanocrystal composites. Nishil Mohammed, **Avijit Baidya**, Vasanthanarayan Murugesan, Anil Kumar Avula, Mohd Azhardin Ganayee, Jyoti Sarita Mohanty, Kam Chiu Tam, Thalappil Pradeep, ACS Sustainable Chemistry & Engineering (2016), 4(11), 6167-6176.

V. Synthesis of silicon nanoparticles from rice husk and their use as sustainable fluorophores for white light emission. Sandeep Bose, Mohd. Azhardin Ganayee, Biswajit Mondal, **Avijit Baidya**, Sudhakar Chennu, Jyoti Sarita Mohanty, Thalappil Pradeep, ACS Sustainable Chemistry & Engineering,(2018), DOI: 10.1021/acssuschemeng.7b04911.

VI. Patterned Nanobrush Nature Mimics with Unprecedented Water Harvesting Efficiency. Depanjan Sarkar, Anindita Mahapatra, Anirban Som, Ramesh Kumar, Ankit Nagar, **Avijit Baidya** and Thalappil Pradeep, submitted.

Patents

I. Aqueous composition for durable and extremely efficient water repelling superhydrophobic materials at ambient conditions. Thalappil Pradeep, **Avijit Baidya**, Mohd Azhardin Ganayee, Swathy Jakka Ravindran, Indian Pat. Appl. 201741036772, 2017.

II. Patterned metallic nanobrushes for capture of atmospheric humidity. Thalappil Pradeep, Depanjan Sarkar, Anindita Mahapatra, Anirban Som, **Avijit Baidya**, PCT/IN2017/050621, 2017.

III. A method of detection of low concentration of analytes by superhydrophobic pre-concentration paper spray ionization mass spectrometry (SHPPSI MS). Thalappil Pradeep, Pallab Basuri, **Avijit Baidya**, Tripti Ahuja, Indian Pat. Appl. 201741047403, 2017.

IV. Cellulose nanocrystal templated iron oxyhydroxide based adsorbent for arsenic removal from water and a device thereof. Thalappil Pradeep, **Avijit Baidya**, Bibhuti Bhusan Rath, Avula Anil Kumar, Indian Pat. Appl. 201641027660, 2016.

V. Method of synthesis of atomically precise metal cluster-cellulose nanocrystal composite for diffusion controlled simultaneous sensing and scavenging of heavy metal ions in water. Thalappil Pradeep, Nishil Mohammed, **Avijit Baidya**, Vasanthanarayan Murugesan, Avula Anil Kumar, Kam Chiu Tam, Indian Pat. Appl. 201641031815, 2016.

CHAPTER 1

Introduction

1.1 Influence of Mother Nature on The Evolution of Science and Engineering

The progress of science is continuous, that is happening each and every moment and even right now. As a collection of tiny water drops can make an ocean, these small steps taken every day have assisted the wheel of technological revolution, so that we are at the place where we are currently. Careful analysis of this path of rapid evolution, one of the biggest milestones achieved by the human being, certainly reveals the influence of Mother Nature in this advancement. Imagination being the greatest power or tool for inventions, Nature has encouraged human beings to think, create and break the barrier to explore new possibilities for the betterment of mankind. This is clearly seen in each and every domain of science and technology (Figure 1.1).

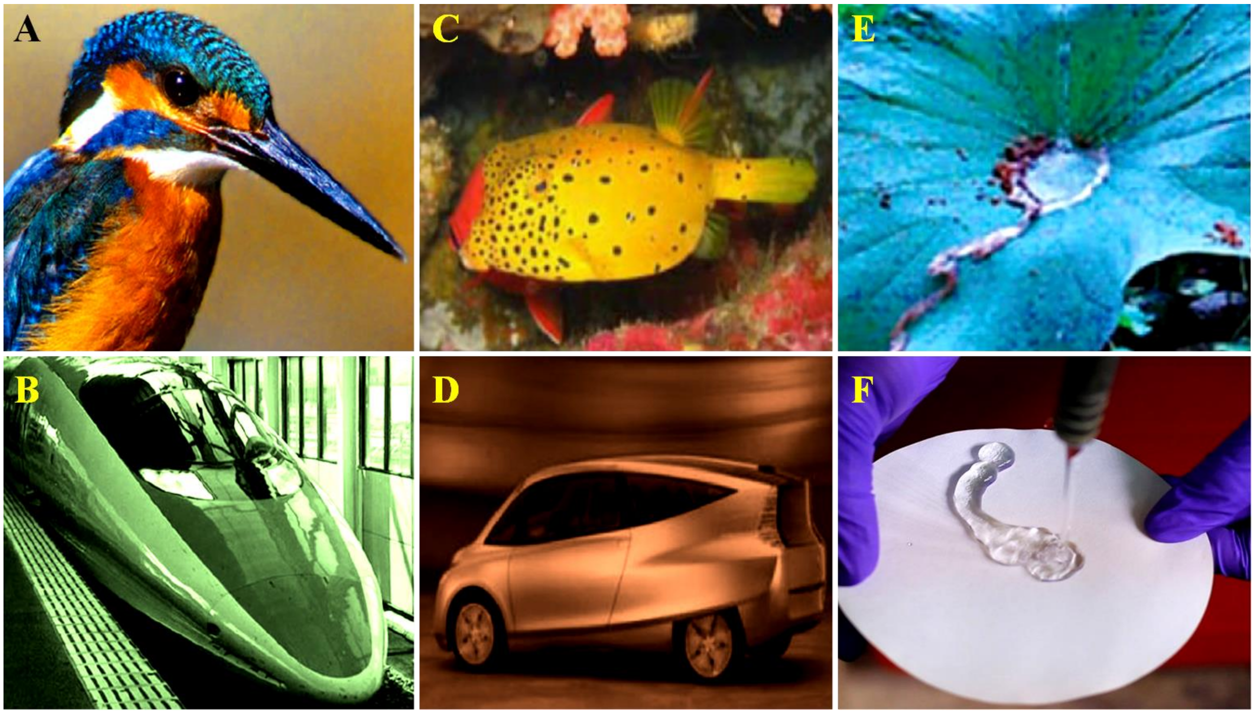


Figure 1.1 (A,B) Kingfisher’s beak-inspired design of high speed train. Reproduced with permission from (Goel, 2013), © 2013 IEEE. (C,D) Box fish-inspired design of vehicle. Reprinted with permission from (Bannasch, 2009) © 2009 Springer

Nature. (E) Water droplets of superhydrophobic lotus leaf surface, inspiration of various new technologies in diverse fields of science and engineering. Reproduced in part with permission from (Wen *et al.*, 2017) © 2017 Royal Society of Chemistry. (F) Artificially developed superhydrophobic surface. Reprinted with permission (Baidya *et al.*, 2018) © 2018 John Wiley and Sons..

Science took the leading role to resolve problem of everyday life. However, its own growth got nutrients from the careful observation of naturally occurred phenomena, widely known as bio-mimicry. People have mimicked several natural processes to develop materials and devices that have a great need for everyday use. Starting from the example of "flying machine" to the fastest bullet train, technologies were built on such careful observations. This was initiated by the great scientist, Leonardo da Vinci (1452–1519) who was a great observer and made numerous notes and sketches of flight of birds to design the "flying machine". Although he failed to make it in reality, later on, Wright Brothers succeeded to make it in the early nineteenth century which was solely inspired from the observations of the flight of pigeons. Likewise, a bunch of examples exist that proves the blending of nature with science. For instance, the invention of small 'hook' which later on translated to the 'velcro' was a pure bio-mimic of burdock burrs (Hargroves and Smith, 2006). Design of turbine blades also came from the wings of humpback whale (Goel, 2013). Designs to reduce the drag of liquid came into the picture from the hierarchal texture of the fish scales (Liu and Jiang, 2011). These explain how developed human mind has appreciated and adopted to the creativity of nature and made innovations. Thus, today, Nature has become an idol for research & development and often named as a celebrity designer. The biomimetic development also facilitated the invention of the display technology through structural colouration rather than pigmentation. This was first observed in the wings of 'Morpo' butterfly that consists of different microstructures which create the colouring effect and is easily explainable with multilayer interference. These structures have also imparted water repelling property to the surface (Zheng *et al.*, 2007; Liu and Jiang, 2011). Such inventions are extended to gecko's feet, known to provide proper grip and adhesion (Autumn, 2011), spider web glass and many others (Liu and Jiang, 2011). There are many more examples of such developments that are still in the processing stage. For instance, flexible robotic arm resembling elephant's trunk, design of cars from the shape of fish, *etc* (Bannasch, 2009). On the other side, scientists are also trying to replicate brain's activity and its networking system by observing the response of neurons through external stimuli. This will certainly enhance the growth of artificial intelligence, widely known as AI, which is believed to make the biggest impact on the world in the history of innovation. Another interesting ongoing development, design of the self-driving car that runs with artificial intelligence, also conceptually follows biomimicry.

1.2 Biomimicry and Surface Engineering

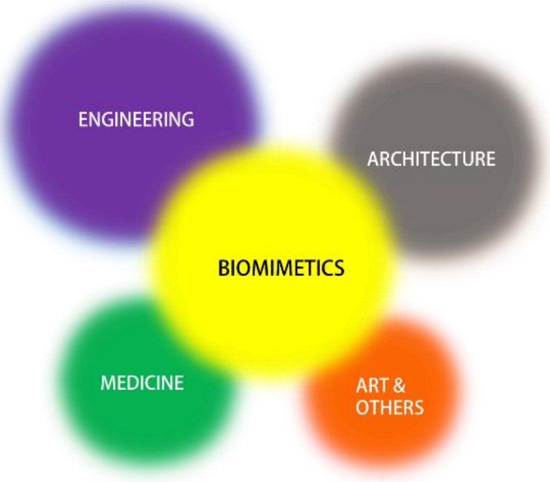


Figure 1.2 Mixing of different areas through biomimetics.

Although the bio-mimetic progress of science towards various technologies is often visible in everyday life, it has also enriched the domain of materials science, architecture, construction, medicine and medical science, economics and many others (Figure 1.2). These are related to the behavior and nature, communication mechanisms, materials related to smallest building blocks, design and construction processes of natural species like plants, insects, and animals. Interestingly, almost in all the cases it has been seen that naturally available biological surfaces are made of different unique geometrical structures and chemical constituents. These are proven to be the governing parameters or factors for several remarkable features of these natural surfaces. Therefore, surface engineering, more precisely mimicking such natural surfaces has become one of the intensely pursued research topics both in academics and industries. Among these, surfaces that show different liquid repelling behavior, for example, various skin, feet, wings, leaf, petals of various biological species, have attracted people because of their immense technological importance (Figure 1.3) (Liu and Jiang, 2011; Darmanin and Guittard, 2017; Wen *et al.*, 2017). This includes several important areas like sensing, self-healing, self-cleaning, coating, water purification, anti-icing, drag reduction, heat transfer, microfluidic devices, smart windows/ glass, *etc.*, where properties of the surfaces play a major role (Liu *et al.*, 2014; Wen *et al.*, 2017). Thus, designing such surfaces which is robust and rugged in nature and provides controlled multi-functional properties are important and have become a mainstream research area in the field of surface modification.

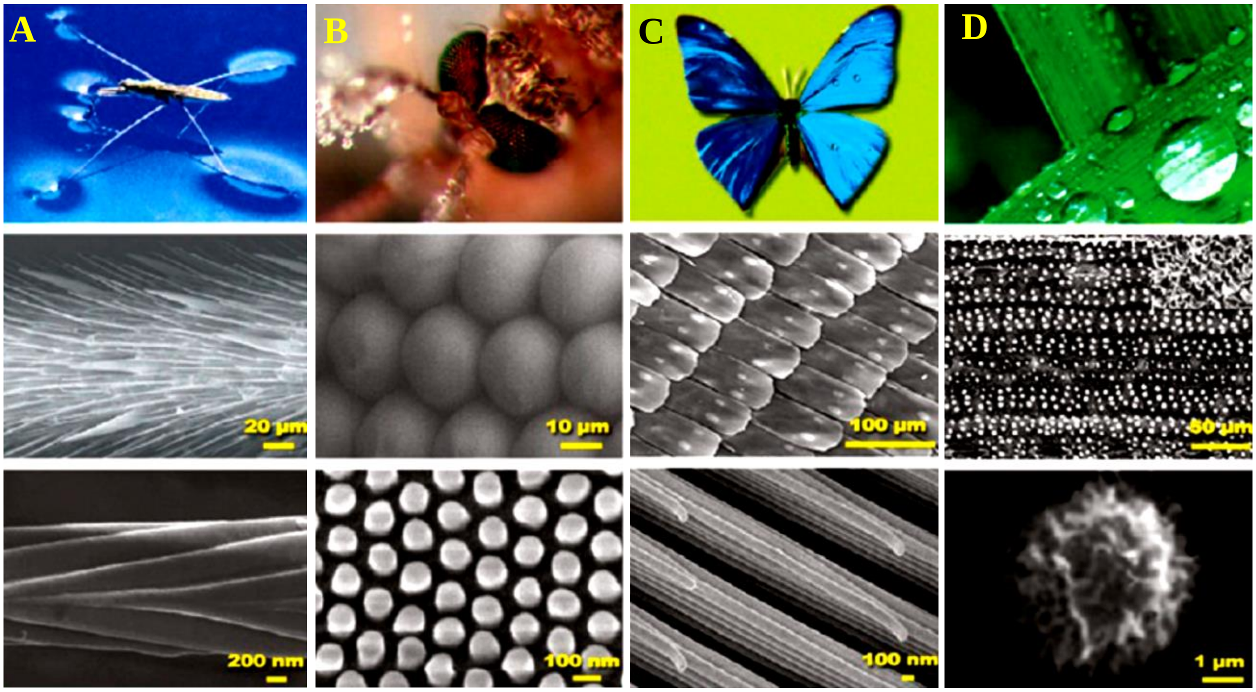


Figure 1.3 Naturally available nonwetting surfaces and their corresponding SEM images. (A) Directional arrangements of needle-like micro-structures on a water strider’s leg that deliver robust and durable superhydrophobicity helping it to stand on water surface. Reproduced with permission from (Gao and Jiang, 2004) © 2004 Nature Publishing Group. (B) Presence of micro-ommatidia covered with nano-nipples control the water repelling characteristics of a mosquito’s eyes. Reproduced with permission from (Gao *et al.*, 2007) © 2007 John Wiley and Sons. (C) Microstructures present in the butterfly wings provide adhesion and superhydrophobicity. Reproduced with permission from (Zheng *et al.*, 2007) © 2007 Royal Society of Chemistry. (D) Directional rolling off of water droplets over the rice leaf. Quasi-1D arrangement of micropapillae are the reason of such phenomenon. Reproduced with permission from (Feng *et al.*, 2002). © 2002 John Wiley and Sons. Reproduced with permission from (Liu and Jiang, 2011) © 2011, American Chemical Society.

1.3 Fundaments and Basics of Non-Wetting Surfaces

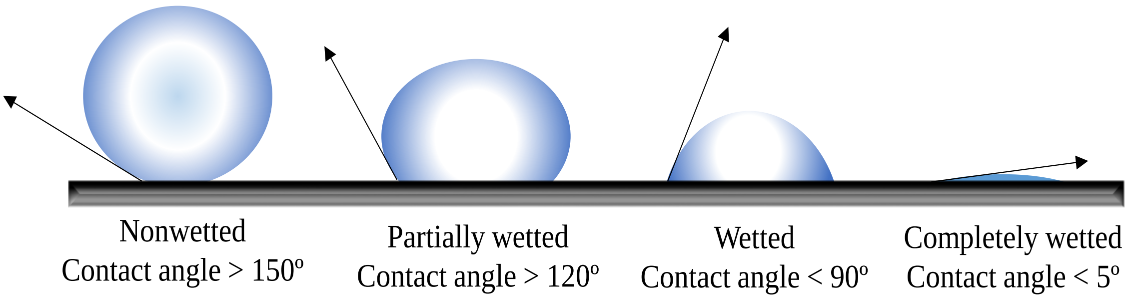


Figure 1.4 Possible wetting behaviour of surface with contact angles.

One of the ubiquitous properties of all the surfaces, in general, is wetting, results from the interaction between liquid and uppermost layers of the substrate (Figure 1.4). It is a macroscopic surface property that can occur in different ways. Mostly, the physical and chemical characteristics of the surfaces control such property. Scientifically or more precisely, the surface energy of the surfaces controls the wetting characteristics. For high surface energy materials, like metals show easy wetting. Whereas, there are various surfaces that possess considerably lower surface energy and are known to show non-wetting characteristics to various extent (will be discussed later).

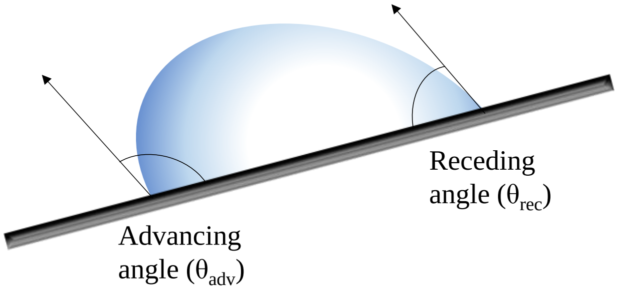


Figure 1.5 Advancing (θ_{adv}) and receding (θ_{rec}) contact angle a tilted surface.

Usually, the contact angle (θ) of the liquid droplets over the surfaces is used as a common quantitative measure of wettability. However, in some cases, the dynamic motions of liquid droplets over the substrate are also used to characterize the non-wetting in detail. Here, the values correspond to the advancing (θ_{adv}) and receding (θ_{rec}) contact angles (Figure 1.5), which are very sensitive towards surface features, play a meaningful role to determine the adhesion of liquid droplets with the surface. Difference between these two parameters is often represented as θ_H, contact angle hysteresis ($\theta_{adv} - \theta_{rec}$) and it is directly related to the sliding angle or roll-off angle (Marmur, 2017).

Generally, these contact angles (θ) are greater than 0° or much less than 180°. Mostly, surfaces, where liquid contact angles of liquid droplets are less than 90° are known as hydrophilic and oleophilic, respectively, for water and other liquids. However, in extreme cases, where contact angle is 0° (known as complete wetting) or very high (known as non-wetting) show interesting phenomena useful for practical applications. Such wetting property is also a function of the surface tension of the used liquids. Sometimes, the non-wetting property of surfaces are also described as liquid repellency and can be categorized in two ways depending on the wetting behavior and the nature of the liquid that we are going to deal with. In the first case, it is known as hydrophobicity where the interaction of water with the surface is considered. The second one is named as oleophobicity where the interaction of other liquids (liquids having lower surface tension value than water) except water is considered. To make it clear, these are named accordingly. When the contact angles of the liquid droplets are greater than 90° the surface is known as hydrophobic (for water) or oleophobic (for all liquid except for water). In some of the cases, the contact angles of the liquid droplets are seen to be greater than 150°. In such cases, these surfaces are named as either superhydrophobic (for water) or superoleophobic (for all liquid except for water). Generally, a surface that shows oleophobicity or superoleophobicity also exhibits hydrophobicity or superhydrophobicity. These surfaces, in particular, are known as omniphobic or superomniphobic (depending on the contact angle) surfaces that repel both water and other liquid at the same time (Marmur, 2008; Hsu *et al.*, 2011; Marmur, 2012; Law, 2014; Marmur, 2017).

Nature has been using several non-wetting surfaces for a long time in many ways to solve its own problems. Neinhuis and Barthlott have first introduced the self-cleaning effect of the lotus leaf, known as lotus leaf effect (Neinhuis and Barthlott, 1997). Authors have well described how these water droplets roll off over the surface and keep the surface (leaf) clean by carrying all the dirt. This helps the leaf to get exposed to the sunlight efficiently. Subsequently, various other natural surfaces came in the light that shows such extreme non-wetting property. Detailed studies have shown that many of these surfaces not only repel water, they restrict other liquids to wet the surface as well with equal efficiency, known as oleophobic/superoleophobic surfaces (Hensel *et al.*, 2013; Nickerl *et al.*, 2013). Droplets of liquids having lower surface tension values also bounce over these surfaces and roll off freely. In view of the liquid repellent property of the surfaces, mostly the shape of the liquid droplets and their movement mechanism over the surfaces, another interesting group of surfaces evolved, known as lubricant-impregnated surfaces (LIS) (Solomon *et al.*, 2017). In this particular case, the surfaces are usually porous and the lubricant fluid stays inside the porous solid matrix. Fluids inside the solid matrices get stabilized by the capillary force (David, 2005; Lafuma and Quéré, 2011; Wong *et al.*, 2011). Liquid droplets (both water and oils) were seen to have relatively lower contact angle and very low contact angle hysteresis, even less than 1° over these surfaces. Unlike the rolling off or bouncing off of liquid droplets over superhydrophobic or superoleophobic surfaces, here liquid droplets slips and shows high mobility. Similar to the previous examples, this one is a bio-mimic of *Nepenthes pitcher* plant (Zhang *et al.*, 2014).

Interestingly, it was observed that all kinds of liquid repelling surfaces contain inherent surface structures and the specific chemical entities. These are proven to be the backbone of this liquid repellent property of these surfaces (In the subsequent sections these will be discussed in detail). To understand the thermodynamic stability of liquid droplets over these surfaces, different functions have been established that explain the solid-liquid-gas interface mathematically, in detail. For smooth and chemically uniform surfaces, the Young equation and the Young-Laplace equation determine the solid-liquid-gas interfacial equilibrium, i.e. the minimum energy state of the system (Marmur, 2017). These two together can explain completely the equilibrium behavior of an interface (Figure1.6A). These are expressed in the following ways:

$$\text{Young equation:} \quad \cos\theta_Y = (\sigma^s - \sigma^{s1})/\sigma$$

Here, σ^s and σ are the surface tensions of the solid and of the liquid, respectively. σ^{sl} is the solid-liquid interfacial tension. θ_Y refers Young contact angle.

$$\text{Young-Laplace equation:} \ P^d - P^c = \sigma(1/R_1 + 1/R_2)$$

P^d and P^c are the local pressure in the liquid droplet and in the continuous phase, respectively. R_1 and R_2 are the radii of curvature of the droplet.

While the former one describes the boundary condition for the shape of the liquid-gas interface in terms of the contact angle, the shape of the interface in terms of the curvature is explained by the Young-Laplace equation, which deals with the local pressure difference across the interfaces. However, when rough surfaces are concerned, two equations are often used to describe the fundamentals of the wettability, namely Wenzel and the Cassie–Baxter equations (Wenzel, 1936; Cassie and Baxter, 1944). In the first case, liquid drops penetrate into the surface roughness and form a liquid-solid interface (Figure1.6B). Here contact angle (θ_w) of the droplets depends on the roughness parameter (r) and is expressed by the equation, $\cos \theta_w = r \cos \theta_Y$. θ_Y is the apparent contact angle.

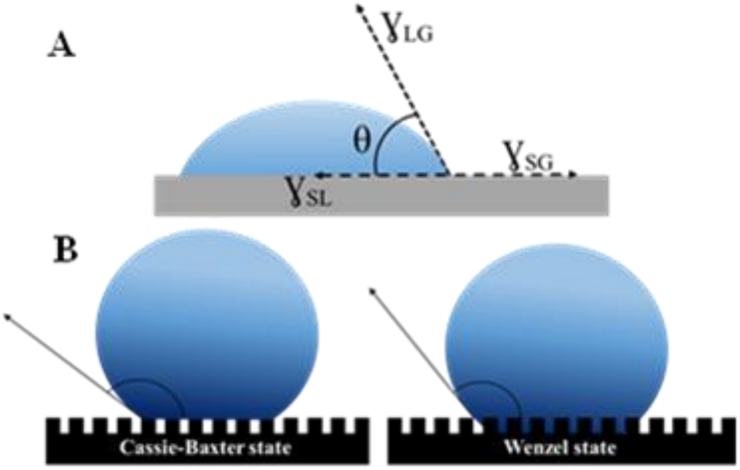


Figure 1.6 (A) Schematic representation of a stable droplet on a surface. Contact angle and corresponding active forces through various interfaces. (B) Contact models of water droplet on the rough surface. Cassie–Baxter and Wenzel state.

For Cassie-Baxter equilibrium, liquid droplets result in partial penetration and stay on top of the surface structures (Figure1.6B). Here, the trapped air between the droplet and the rough substrate remain as it is. The Cassie–Baxter equation is $\cos \theta_{CB} = (r_f \cos\theta_Y+1)f-1$. Here, r_f corresponds to the roughness ratio of the substrate, wetted by the liquid drop, f is the area fraction of the wetted part of the solid surface. Therefore, the true area fraction of the liquid-air interface is $(1-f)$. This is assumed to be flat since the radius of curvature is generally very large compared with the distance between the protrusions of the roughness. Sometimes these two states (Wenzel and the Cassie–Baxter state) are also named as sticky state and slippy state, respectively. Most of the time, surfaces or substrates that are hydrophobic (θ_Y for water > 90°) in nature shows oleophilicity (θ_Y for oils < 90°), especially to low surface tension oils. In such cases, only the Cassie-Baxter state can predict superoleophobic properties of the surface where a large amount of trapped air is essential between the protrusions of the roughness (Darmanin and Guittard, 2017). Therefore, the parameters related to these geometrical structures such as the size of the structures, size of the overhangs, and the distance between the structures are very important to fabricate oleophobic or superolephobic surface. It was shown that surfaces having re-entrant curvatures such as convex microstructures, pillars with overhangs, or mushroom-like structures provide a great increase in oil-repellent property (Cao *et al.*, 2007; Nosonovsky, 2007; Whyman and Bormashenko, 2011).

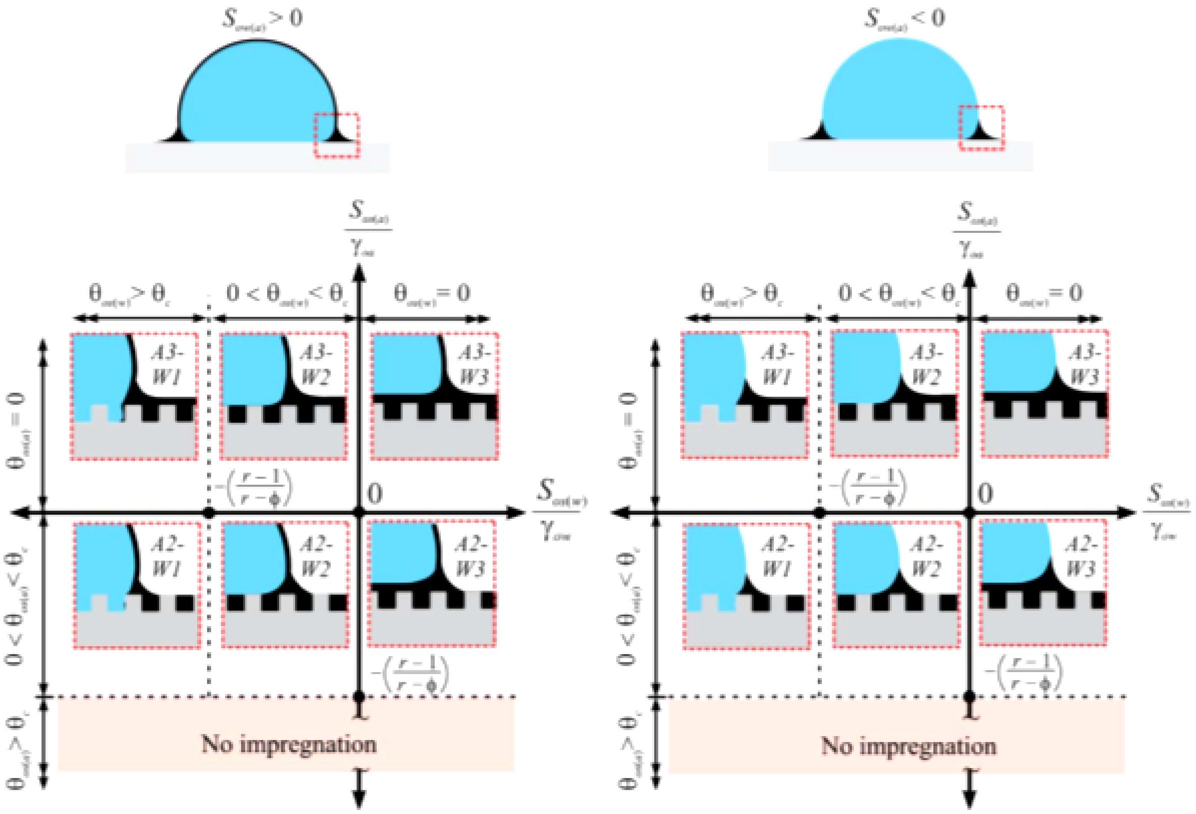


Figure 1.7 Possible thermodynamic states of water droplet on a lubricant-impregnated surface. The top two schematics show whether the droplet gets cloaked by the lubricant. Depending on wetting characteristics of the lubricant in the presence of air and water, six possible states are presented for each case. Reproduced with permission from (Smith *et al.*, 2013) © 2012 Royal Society of Chemistry.

While these surface structures and structural parameters are proven to be so important to impart the liquid repellent property to surfaces, physical and chemical characteristics of the lubricating fluid also play a great role to determine the slip features of the lubricant-impregnated surfaces (LIS) (Solomon *et al.*, 2017). In fact, the interaction between this lubricant fluid with the working fluid and the substrate is known to be one of the important key parameters to obtain the thermodynamic stability or equilibrium of the droplets over this surfaces (Smith *et al.*, 2013). Unlike a single three-phase contact line (interface of liquid-air-solid) for a droplet over the solid surface, the interface of the working fluid and lubricant-impregnated surface is observed to be more complex and shows various exciting properties like anti-icing, condensation, anti-fouling, self-cleaning, increased mobility, *etc* (Solomon *et al.*, 2017). This inspires researchers to investigate the science behind this interfacial phenomenon. Recently, Smith *et al* have shown that depending on the nature of the working fluid droplet, lubricating fluid, solid porous texture, and surrounding ambients a droplet can form 12 different thermodynamic states and constructed a phase diagram of the possible morphology of interfaces between working fluid and lubricant-impregnated surfaces (Smith *et al.*, 2013). Based on the wetting fashion of the working fluid over LIS, three distinctly different states are possible when the interface underneath the droplet is considered. Figure 1.7 shows different possibilities of having various thermodynamic states while a droplet is placed over a LIS. These states are directly related to the interfacial energy. Here, the interaction between the molecules of the working fluid and lubrication fluid also imparts a significant role to stabilize the system. As mentioned in the article, in the first possible case, working fluid drop placed over the lubricant-impregnated surfaces can displace the lubricating fluid completely and forms a direct contact with the solid surface everywhere under the droplet. This phase can be compared with the Wenzel state on a superhydrophobic surface where droplet penetrates inside the microstructure and is named as an impaled state. In the next case, lubricant fluid remains inside the porous matrix but the working fluid drop gets in contact with the exposed solid surface only. This phase is known as impregnated, emerged state. In the last case, working fluid drop does not come in direct contact with the solid surface and sits over the thin layers of the lubricating fluid. Equilibrium thickness of the film depends on the intermolecular force between the lubricating molecules. This particular state is referred as an encapsulated state. The extent of slipperiness was observed to be the highest in this case compared to others. Whereas the first one, impaled state, shows the least slipperiness. Development of such a surface also needs a proper methodology to impregnate the lubricants. Withdrawal of the porous or structured surfaces from the bath of lubricant is frequently used in this context. This is well demonstrated by Seiwert *et al*. with a well-defined micro-pillared surface (Seiwert *et al.*, 2011). Meanwhile, based on the spreading characteristics of the lubricating fluids over the solid surface in presence of working fluid drops, various other morphological scenarios are possible which were subsequently discussed by Smith *et al* (Smith *et al.*, 2013). It is well studied that the combination of lubricating fluids and solids that possess lower surface energies usually forms a stable lubricant-impregnated surface. In this perspective, use of different fluorinated polymers (poly-tetrafluoroethylene and many others), silicone oils and fluorinated oils are well known. Methodologies to develop various textured low surface energy solids are well described in several review articles, for example, the recent review

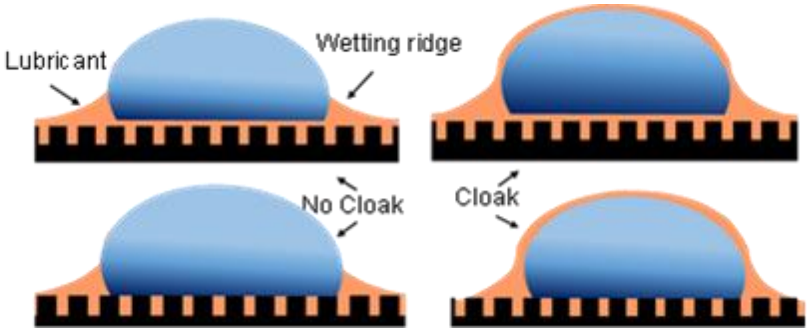


Figure 1.8 Schematic presentation cloaking and ridge on a slippery lubricant-infused surface.

article by Newton and coworkers (Roach *et al.*, 2008). To develop slippery surfaces, liquids having low vapour pressure are more preferred as the evaporation of lubricating fluids can result in a decrease of the performance of these surfaces (Zhang *et al.*, 2014). Placing of the working fluid droplet over the liquid impregnated surface sometime causes spreading of the lubricating fluid over the working fluid droplet or formation of a ridge of lubricant around the working fluid droplets. These are known as cloak and wetting ridge, respectively (Shanahan and Carre, 1995; Bergeron and Langevin, 1996; Carré *et al.*, 1996; Cheng *et al.*, 2014). Figure 1.8 schematically represents possible cloaking and wetting ridge configurations over LIS. This phenomenon was studied in detail and imaged through various techniques like confocal microscopy (Schellenberger *et al.*, 2015), scanning electron microscopy (Rykaczewski *et al.*, 2012; Anand *et al.*, 2015), *etc.* Overfilling of solid surface with lubricant often cause this ridge morphology (Wong *et al.*, 2011). However, in these cases, contact angle hysteresis along with the sliding movement of the water were seen to improve significantly (Kim *et al.*, 2013; Zhang *et al.*, 2014).

1.4 Naturally Available Non-Wettable surfaces

The journey of liquid repelling surfaces was started only two decades back with the report of non-wettability of the lotus leaf (Neinhuis and Barthlott, 1997) and the scientific explanation of this phenomenon was revealed nearly about half a century ago (Cassie and Baxter, 1944). Water droplets were seen to bounce and roll off easily over the surface of lotus leaves and keep them dry and clean from dirt and mud which is referred as the lotus leaf effect. Rolling off of this water drops, even with a small tilted angle, resembles frictionless movement. Such an excellent water-repelling property eventually triggered the development of artificial surfaces of this kind. Subsequently, this phenomenon has been extended to various liquids, ice and fog repelling surfaces and has enriched various domains of science and engineering. Such surfaces include glass, textiles, oil-resistant clothing, anti-smudge surfaces, displays, anti-icing coatings automobiles and aircraft and anti-corrosion coatings for different metal bodies and the use of this phenomenon has been applied to liquid transportation systems, atmospheric water capture, oil-water separation, waterproof electronics, sensing and many others (Amirfazli and Antonini, 2017; Baidya *et al.*, 2017; Ju *et al.*, 2017; McHale, 2017; Post *et al.*, 2017; Wen *et al.*, 2017).

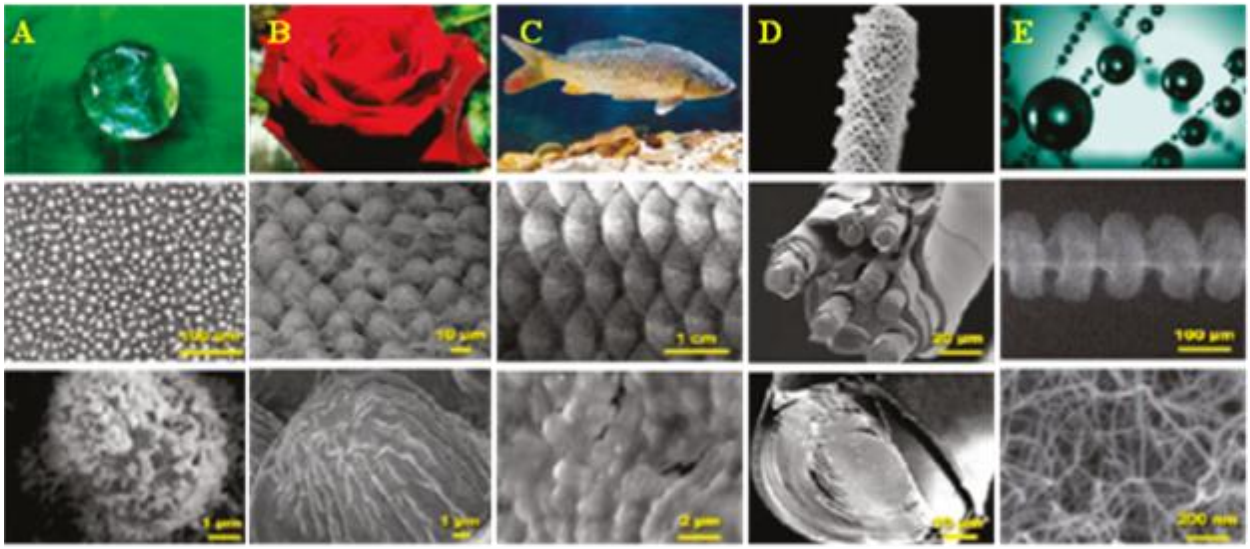


Figure 1.9 Naturally available non-wettable surfaces of various biological species. (A) Lotus leaf (superhydrophobic, low adhesive, and self-cleaning properties). Reproduced with permission from (Feng *et al.*, 2002) © 2002 John Wiley and Sons. (B) Red rose petals (superhydrophobicity with high adhesion). Reproduced from (Feng *et al.*, 2008) © 2008 American Chemical Society. (C) Fish scales (drag reduction, superoleophilicity in air, and superoleophobicity in water). Reproduced with permission from (Liu *et al.*, 2009) © 2009 John Wiley and Sons. (D) Spicules (mechanical and fiber-optical properties. Reproduced with permission from (Sundar *et al.*, 2003; Aizenberg *et al.*, 2005) © 2003 Nature Publishing Group and © 2005 AAAS, respectively. (E) Spider capture silks (superior water collection ability, mechanical property, elasticity, and adhesiveness). Reproduced with permission from (Zheng *et al.*, 2010) © 2010 Nature Publishing Group. Reproduced with permission from (Liu and Jiang, 2011) © 2011, American Chemical Society.

1.4.1 Hydrophobic Surface

To understand the superhydrophobic property of lotus leaves, surface anatomy of this surface has been studied in great detail. It was observed that surface of lotus leaf contains duel scale micro and nanostructures along with a wax-cellulose composite (Neinhuis and Barthlott, 1997). This micro-nano structure helps to trap air which has proven to be the governing factor of such phenomenon. Similar to this lotus leaf, several other biological surfaces (both plants and animals) are also observed to show hydrophobicity (Figure 1.9) such as rose petal, peanut leaves, rice leaves, cicada wings, mosquito eye *etc.* (Liu and Jiang, 2011). Jiang *et al* have shown the presence of needle-shaped microstructures on water strider's leg which contributes to the easy and rapid movement of these species over the water surface (Gao and Jiang, 2004). Barthlott's group has studied almost 97 wings of insects and found that various families including mayflies, butterflies, stoneflies, lacewings, alderflies, scorpionflies, caddisflies and dragonflies, show hydrophobic property to different extent (Darmanin and Guittard, 2015). Among these, some surfaces were seen to have high water contact angle with large adhesion force which restricts the rolling off of water drops. One of the well-known examples of high adhesion superhydrophobic surface is gecko's feet. Hairy structured surface of gecko's feet helps them to walk even through a vertically smooth surface. Autumn and coworkers have shown that van der Waals interaction is working between these structured surface (gecko's feet) and the molecules of the surface (on which they are moving) which controls this phenomenon (Autumn *et al.*, 2000; Autumn, 2011).

1.4.2 Oleophobic Surface

Thinking about the main drawback of superhydrophobic surfaces, it was found that these surfaces are highly selective towards liquids. For example, particularly in the case of the lotus leaf, although it shows excellent superhydrophobicity, i.e., having water contact angle greater than 150°, it gets wet readily with organic solvents that possess lower surface tension than water. This facilitates the development of oil repellent surfaces named as oleophobic surfaces. Similar to the previous one, in nature, various surfaces of both plants and animals exist that offer such properties. For example, many species of Collembola (springtails) (Figure 1.10) and leafhoppers (Insecta, Hemiptera, Cicadellidae) are well-known examples of such surfaces and have been studied in detail (Nickerl *et al.*, 2013; Darmanin and Guittard, 2017; Wu *et al.*, 2017).

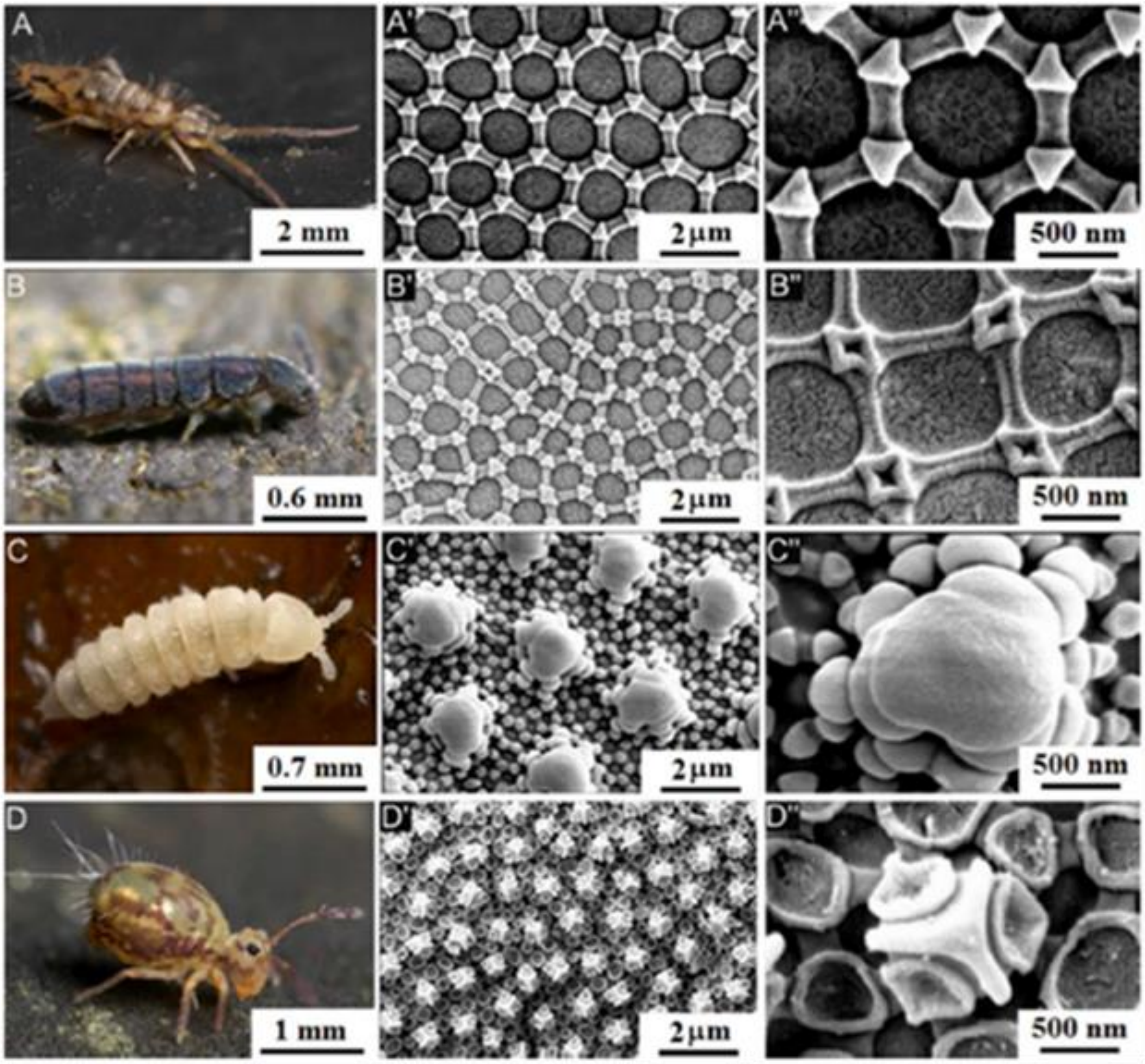


Figure 1.10 Naturally available oleophobic surfaces, various species of Collembola. (A) Epedaphic Entomobryomorpha. (B) Hemiedaphic Isotomidae. (C) Euedaphic Poduromorpha and (D) Hemiedaphic Symphypleona. Reprinted with permission from (Nickerl *et al.*, 2013) © 2013 Springer Nature.

In this case also, structural aspects along with the chemical components of these surfaces control wettability. For instance, in the first case, the presence of highly ordered hexagonal comb like patterns restrict the surface to get wet by oils. Later on, based on the details of these structures, researches have tried to incorporate similar liquid repellent property to the surface to solve various potential problems of today. Recently, Wu and coworkers have fabricated highly ordered re-entrant surface that shows both superhydrophobicity and superoleophobicity alone with remarkable self-healing property (Wu *et al.*, 2017).

1.4.3 Slippery Surface

Development of the slippery surfaces or lubricant-impregnated surfaces was started with the inspiration of Nepenthes pitcher plants (Zhang *et al.*, 2014) where liquid drops slip, and do not roll off. With time, researchers have designed several of such surfaces in various ways (Solomon *et al.*, 2017). Recently, Aizenberg and coworkers have demonstrated the formation of such a slippery surface having exceptional antifouling property (Epstein *et al.*, 2012). Similar to this, a bunch of examples of such surfaces are known which have lots of applications in different field science and technology (Solomon *et al.*, 2017).

Figure 1.11 Photograph of Nepenthes pitcher. Reproduced with permission from (Zhang *et al.*, 2014) © 2014 John Wiley and Sons.

1.5 Artificially Fabricated Non-Wettable Surfaces

From the recent past, a great effort has been made by the researchers to develop naturally evolved surface structures to induce certain important properties to the surfaces (Bayer, 2017; Franssila, 2017; Law and Zhao, 2017; Ueda and Levkin, 2017). In this context, different approaches have been introduced irrespective of the expense, patternable surface area, roughness parameter (length scale, such as micro, nano or micro-nano scale), industrial viability, material's compatibility, adopted techniques and eco-friendliness. Ideally, it should be similar to the nature's ways of making such important architectures that involve only a few simple conditions like environmental temperature, atmospheric pressure, water as a solvent system and biologically available nontoxic chemicals. However, these structures are highly uniform, accurate, maintains periodicity, excellent robust in nature, inertness towards different environmental conditions and furthermore, possess long standing durability. These make these systems beautiful and more attractive. In view of the techniques to fabricate such structures in order to implement such excellent non-wettability to the surfaces, it can be divided in two ways in a broad sense.

1. Top-down approach: Here various etching processes, lithographic techniques and many others are used to produce different micro/ nanostructures over the surfaces of interest. Usually, non-wetting property of the surfaces are introduced through various low surface energy molecules. Depending on the regularity and the length scale of required structures or roughness, respective techniques are introduced.
2. Bottom-up approach: In this case, various chemical functionalization procedures are used to design low surface energy materials. Either these materials are directly grown over the substrates or separately prepared material gets coated over the surfaces of interest. Size and shape of the matrix that gets functionalized (like different nanoparticles or fibers and so on) and the chemical functional groups of the reagents play an important role.

1.5.1 Top-Down Approaches

Learning from the natural examples and the detailed understanding of the fundamental theories of non-wettability together have shown/demonstrated the importance of the structural aspect to design superhydrophobic surfaces. With time, different processes have introduced to fabricate such structures over various substrates. Often these approaches are called as a top-down approach as the bulk materials get structured through the process of different lithographic techniques, and so on. These are very expensive, difficult and need complex processing steps (Choi *et al.*, 2008; Franssila, 2017). Several research groups have demonstrated the formation of such ordered nanostructures that show excellent water as well as oil repellency. However, it is observed that fabrication of a random micro surface roughness or structures through various etching techniques over large area surfaces is relatively easy and cost-effective to implement. Mostly, depending on the substrates these respective methodologies are used. For example, in case of metal surfaces acidic etching is used, for polymer-based or silicon or silica substrates, plasma etching procedures are useful. Use of electrochemical etching and metal-assisted wet chemical etching process are also known to impart random roughness of the metal and silicon substrates (Franssila, 2017).

1.5.1.1 Plasma Etching

Plasma etching is one of the frequently used processes to import different length scale structures on a given substrate. It is a dry technique to develop controlled surface structures with the help of reactive atoms or ions. Power, flow rate, temperature, pressure, flow gas are the main parameters of this etching process. Because of the high reactivity towards the substrates, fluorine (F_2) and oxygen (O_2) gases are often used for the etching process. However, reports exist where Cl_2 and Br_2 are used, although these need ion assistance and provide lower performance, nearly 10% compared to the F_2 (Franssila, 2017). Use of various other gas sources such as fluorinated species (tetrafluoromethane), ammonia, and argon are also known in this context and introduce different functionality over the surfaces. For example, Fresnais *et al* have shown the formation of low-density polyethylene based superhydrophobic surface that showed high water contact angle and low hysteresis. Here, to obtain the water repelling features, the surface was treated with oxygen and CF_4 plasma, sequentially (Fresnais *et al.*, 2006). Plasma treatment of polymeric materials can change the chemical property of the polymer along with the surface roughness of the substrates. Recently, Chen *et al*. have reported the formation of the superhydrophobic surface from a plasma treated superhydrophilic surface (Chen *et al.*, 2016).

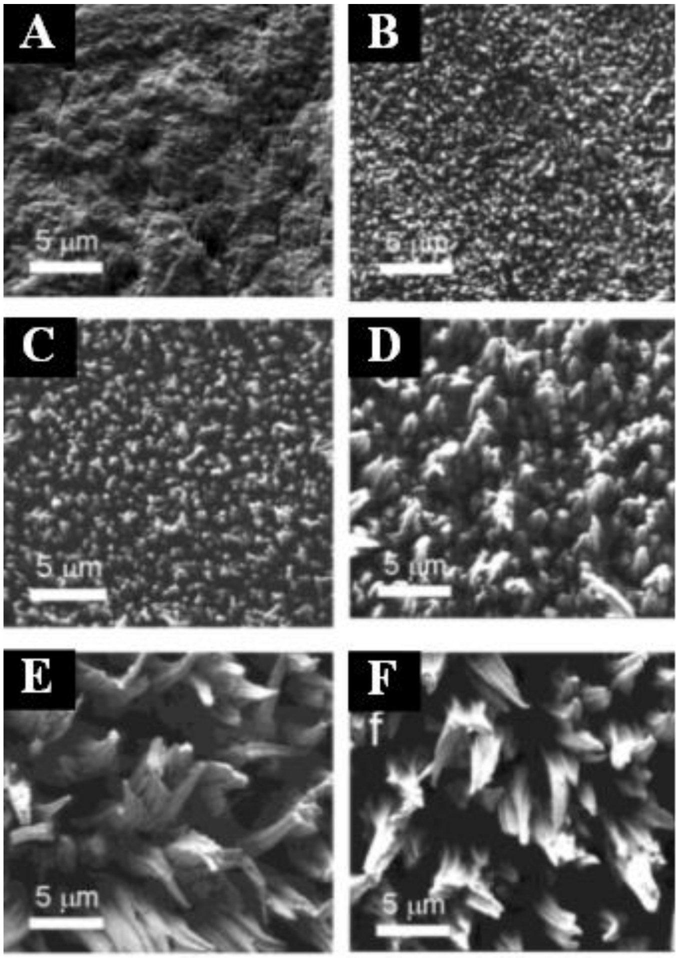


Figure 1.12 SEM images of PTFE foils after time dependent plasma treatment. (A) Untreated (B) 60 s, (C) 120 s, (D) 5 min, (E) and 10 min. (F) Oxygen plasma for 10 min+NH_3 for 1 min. Reproduced with permission from (Minko *et al.*, 2003) © 2003, American Chemical Society.

Oxygen plasma treated superhydrophobic Poly(tetrafluoroethylene) (PTFE) surface was developed by Stamm and coworkers. Later on the etched surface was treated with ammonia plasma to introduce the amine functionality to the surface. These amine groups eventually helped to further modification with carboxyl-terminated polymers namely, poly(styrene-co-2,3,4,5,6-pentafluorostyrene) and carboxyl-terminated poly(2-vinylpyridine), which controlled the solvent dependent switching of wettability of the surface (Figure 1.12) (Minko *et al.*, 2003).

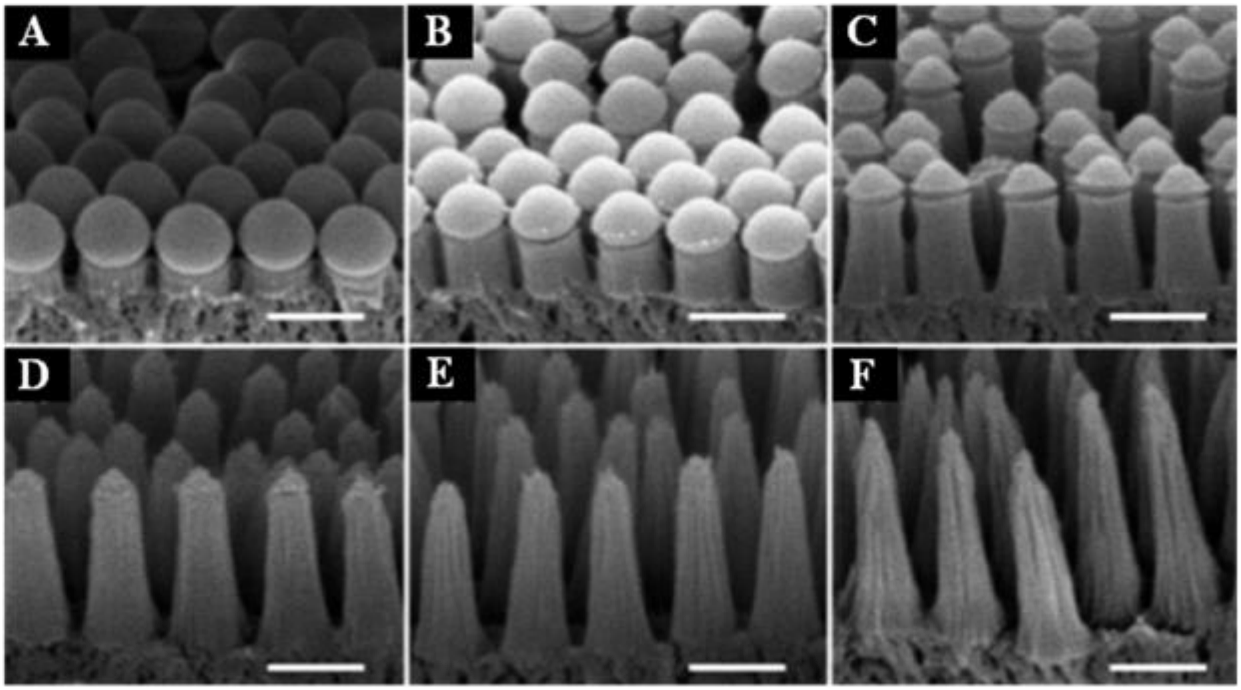


Figure 1.13 Morphology of the surface after explosion for different etching times. (A) 50 s, (B) 100 s, (C)150 s, (D) 200 s, (E) 250 s, (F) 300 s. Scale bar: 500 nm. Reproduced with permission from (Wang *et al.*, 2015) © 2015 Royal Society of Chemistry.

Use of plasma to activate the polymerization of fluoroacrylic polymer was introduced by McCarthy and coworkers (Chen *et al.*, 1999). Similar mechanism was used by Ucar *et al*. where plasma enhanced chemical vapor deposition (PECVD) technique was used to form a thin layer of poly(2,2,3,4,4,4-hexafluorobutyl acrylateglycidyl methacrylate) (P(HFBA-GMA)) over the fibrous matrix. Low surface energy of this polymeric thin film showed excellent non-wetting property with unchanged breathability (Karaman and Uçar, 2016). In several cases, a combination of different techniques was used to fabricate superhydrophobic surfaces. For example, a combination of colloidal lithography and O_2 plasma etching was used to develop a hierarchical hair-structured superhydrophobic polymethylmethacrylate (PMMA) surface having polystyrene

(PS) spheres over these aligned pillars (Wang *et al.*, 2015). Figure 1.13 shows SEM images of these hairy structures evolved with different etching time. Rod structured superhydrophobic surface was made by Kim and coworkers where the fabricated surface was chemically functionalized with fluorocarbon molecules separately (Cho *et al.*, 2016). Similar to these, several other examples of superhydrophobic surfaces are known where plasma method was used extensively (Wu *et al.*, 2003; Wu *et al.*, 2003; Wu *et al.*, 2004; Teshima *et al.*, 2005; Li *et al.*, 2007).

In some of the cases, to enhance the selectivity and the rate of etching, powerful (kW) radiofrequency (RF) sources are used to produce the high-density plasma that generates ions. Size of the ions produced in this process mostly governs the selectivity (Wu *et al.*, 2010). This is referred as deep reactive ion etching (DRIE) and use in Bosch process. Here, SF_6 and C_4F_8 are used in cyclic fashion for the etching and passivation (Nguyen *et al.*, 2014). Cryogenic DRIE requires very low temperature around -100 °C to -120 °C and simultaneous replenishing of passivation layers. This process is similar to the Bosch process having low etching rate (Sainiemi and Franssila, 2007). Solomon *et al* have reported the development of the superhydrophobic surface through a DRIE process that contains submicrometer scale pillar structures (Krupenkin *et al.*, 2007). Meanwhile, Franssila *et al* also have demonstrated the formation of 20-micrometre tall silicone pillared surface through cryo DRIE process (Sainiemi *et al.*, 2008). Isotropic etching being essential to develop overhang pillar structures that shows excellent superoleophobicity, recently, Houselt *et al* have reported the development of pillar structured silicon surface that repels oils having low surface tension like n-octane (Susarrey-Arce *et al.*, 2013).

1.5.1.2 Templation Technique

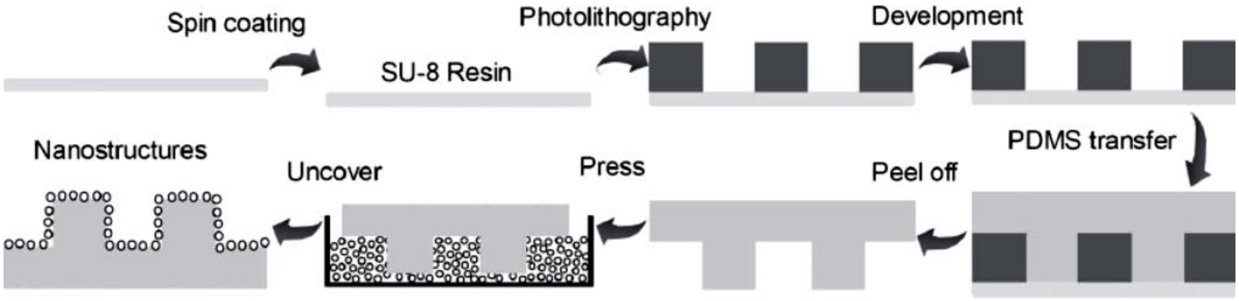


Figure 1.14 Schematic representation of the fabrication process of artificial rice leaf. Reproduced with permission from (Wu *et al.*, 2011) © 2011 John Wiley and Sons.

Templation is known as one of the oldest methods for replication of different structures. It requires a well-defined template that will be replicated through the subsequent steps. Finally, the careful removal of the template by lifting or dissolution through an appropriate solvent results in the negative replica of the template having the desired features (Li *et al.*, 2007). Usually, polymeric materials are used to develop the mold which later on gives the identical structures that were present in the template (Wen *et al.*, 2017). Several naturally available surfaces having different structures including lotus leaf (Sun *et al.*, 2005), grasshopper wings, rice leaves are used as a template to develop liquid repelling surface through this method. Use of artificially made templates, for example, membrane, lithographically made patterned surfaces are also known. However, developing structures of naturally available surfaces having nm length scale features, for example beyond 5 nm, is really difficult (Jin and Kim, 2011). Recently, Jiang *et al* have demonstrated the preparation three level microstructured (macro/micro/nano) patterned surface to mimic the anisotropic sliding of water droplets over the rice leaf. Figure 1.14 shows the schematic representation of the fabrication procedure. Detail experiments on sliding angles confirmed that such structural arrays inherently controlled the anisotropic sliding over the surfaces (Wu *et al.*, 2011).

The same group have fabricated grasshopper wings patterned polydimethylsiloxane (PDMS) surface through this templation method (Zhang *et al.*, 2011). Pisignano *et al* have used *Strelitzia reginae* leaf as a template. Both the dried and green leaf of the species were used for replication and compared (Mele *et al.*, 2012). Microstructured porous candle soot templated transparent superamphiphobic surface was prepared was reported by Vollmer and coworkers. Fabricated surface showed excellent durability and remain functioning even even when the top few layer was removed (Deng *et al.*, 2012). Figure 1.15 shows the deposited carbon soot, silica nanoparticle coated soot and the morphology of the substrate after removal of carbon by heating at 600 °C for 2 hours. Chen *et al*. have shown the development of the lotus leaf mimic structure. Here, PDMS was used to prepare the negative replica of the lotus leaf and used as a master to fabricate the positive replica. Even the inherent nanostructures along with the microstructures of the leaf were preserved in the developed surface and showed excellent superhydrophobicity having a water contact angle 160 (Sun *et al.*, 2005). Similar approaches were made by Lee *et al* to fabricate relatively bigger structures with a separately fabricated patterned surface (He *et al.*, 2003). Rodriguez *et al*. have fabricated superhydrophobic surface where anodized aluminium substrate was used as a template (Ho *et al.*, 2014). During the process, this nanoporous membrane was nanoimprinted over a thermoplastic material to obtain the water repelling surface. Recently, use of hierarchical nanostructured porous hydrogel matrix as a template to fabricate superhydrophobic surface was demonstrated by Yu *et al* (Wang *et al.*, 2014).

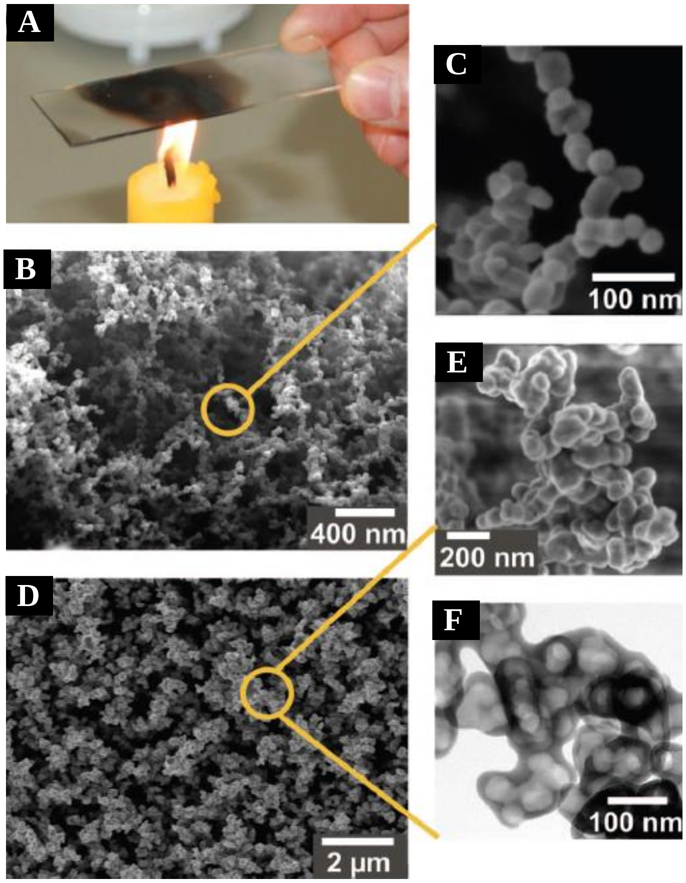


Figure 1.15 (A) Photograph of sample preparation. Few micron thick soot deposited on a glass slide. SEM image of the (B,C) deposited soot and (D) after being coated with a silica shell. (E,F) High-resolution SEM and TEM images of a cluster after removing the carbon core by heating for 2 hours at 600°C. Reproduced with permission from (Deng *et al.*, 2012) © 2012 AAAS.

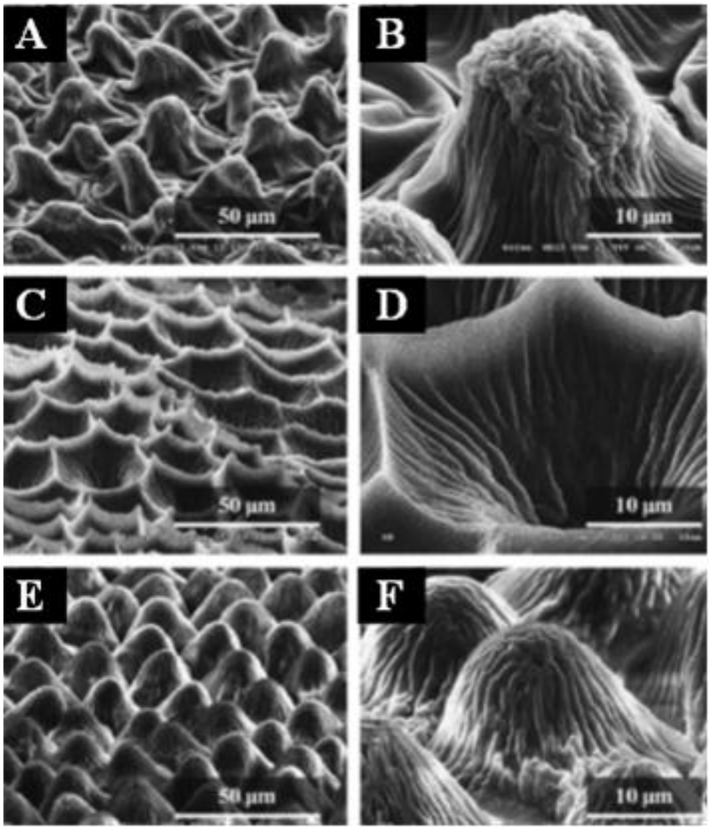


Figure 1.16 SEM images of (A,B) rose petal,(C, D) first rose-petal replica, and (E, F) second replica. Reprinted with permission from (Choo *et al.*, 2014) © 2014 Elsevier

In some of the cases, replication of the patterns over thermoplastic polymeric matrixes are performed with pressure and temperature treatment, known as nanoimprint lithography (Guo, 2004). Here, the polymers were pressed above the glass transition temperature to make the structures. This method is capable to replicate even nanometer scale fine structures in the depending on the design of the master. Recently, Lee *et al*. have developed rose-petal structured superhydrophobic surface having water contact angle 144°. Particularly in this method, UV-nanoimprint lithography technique was used to develop such nanostructures over perfluoropolyether (PFPE) surface (Choo *et al.*, 2014). Figure 1.16 shows the SEM images of rose petal (A,B), first replica (C,D) on polyurethaneacrylate (PUA) and the second replica (E,F) on (PFPE) (prepared by UV-nanoimprint lithography). Use of capillary force during the templation method is demonstrated by Suh and Jon. Here, the patterned mold was directly put on the poly(ethylene glycol) (PEG) coated film (Suh and Jon, 2005). Similar approaches have been made by Jiang *et al* to prepare aligned nanotube structured polystyrene surface which shows superhydrophobic property with sticky characteristics, i.e. water droplets do not roll off even after making the surface upside down (Jin *et al.*, 2005). Recently, Ag nanocube incorporated micro-patterned surface was made through capillary force lithography that shows surface-enhanced Raman scattering (SERS) with excellent superhydrophobicity (Rui Tan *et al.*, 2014).

1.5.1.3 Photolithography Technique

Similar to templation techniques, photolithography technique also includes several steps where irradiation of the light through the mask plays the most important role to develop the structures. Depending on the necessity, different light source like electron beam, X-ray *etc* and photoresist are used during the patterning process (Li *et al.*, 2007; Chen *et al.*, 2017; Darmanin and Guittard, 2017; Law and Zhao, 2017). Furstner *et al*. have developed spike patterned silicon surface through the X-ray lithography. Later the surface energy of the surface was controlled by solution immersion process where gold sputtered patterned surface was dipped in the hexadecanethiol solution (Fürstner *et al.*, 2005). Electron beam lithography was used by Martines *et al* to fabricated nano pillars and nanopits patterned hydrophobic surface on silicon. Dependency of non-wettability on spacing parameter and aspect ratio of the pillars are demonstrated here (Martines *et al.*, 2005). Several other reports exist that demonstrated the photolithographically development of different liquid repelling surface. This reveals the richness of this subject area.

1.5.2 Bottom-Up Approaches

Developing or designing liquid repellent (hydrophobic/ superhydrophobic/ oleophobic/ superoleophobic) materials through chemical modification, has become one of most commonly used technique in past few years. It provides wide applicability of these materials over a diverse array of substrates in a large area. Usually, these materials are prepared in suitable organic solvents as low surface energy molecules get soluble in nonpolar liquid. Use of various inorganic (metal oxide nanoparticles, clays, carbon derivative materials *etc.*), organic (different polymeric materials, cellulosic materials, *etc.*) and hybrid materials (composite material) are well-known and frequently used to formulate these liquid repelling materials (Li *et al.*, 2007; Chen *et al.*, 2017; Wen *et al.*, 2017).

1.5.2.1 Direct Coating of Chemically Modified Materials

In the view of the methods to fabricate superhydrophobic surfaces, in comparison to other bottom-up processes, coating method is known to be the most widely adopted techniques to develop non-wettable surfaces. The process can be as simple as to immerse the substrate in an as-prepared material or coating of as-prepared material by available coating techniques such as spray coating, brush coating, dip coating and many others depending on the nature of material, solvent and substrates (Geissler *et al.*, 2013; Deng *et al.*, 2014; Guo *et al.*, 2015; He *et al.*, 2015; Kim *et al.*, 2015; Li *et al.*, 2015; Si *et al.*, 2015; Yu and Guo, 2015; Zhou *et al.*, 2015; Cao *et al.*, 2016; Wang *et al.*, 2016; Wang *et al.*, 2016; Wang *et al.*, 2016; Xu *et al.*, 2016). More often different kind of functionalized dispersed particles, metal/metal oxide nanoparticles, various inorganic materials are synthesized chemically and get coated over the substrates (Hou *et al.*, 2015; Boakye-Ansah *et al.*, 2016; Wang *et al.*, 2016). For instance, Yoon *et al* have reported the formation of the transparent superhydrophobic glass surface that shows excellent robustness and self-cleaning property. Here, the glass surface was coated with functionalized alumina particles made in alcohol (Figure 1.17). Depending on the amount of the material coated over the surface, wettability as well as the transparency change (Yoon *et al.*, 2015).

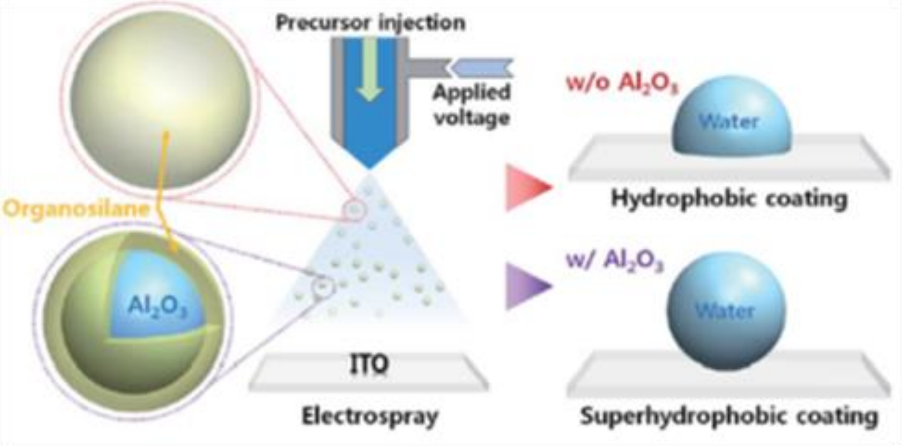


Figure 1.17 Schematic for the preparation of superhydrophobic coatings. Reproduced with permission from (Yoon *et al.*, 2015) © 2015 Royal Society of Chemistry.

Similarly, Pei *et al* have fabricated superhydrophobic paper having excellent chemical stability through a dip coating procedure. In this case also chemical modification of the SiO_2 nanoparticles was done in ethanol (Tang *et al.*, 2013). Carbon nanotube-based superhydrophobic surface was prepared by Lin *et al*. where carbon nanotubes were dispersed in polyamine and finally cured with resin over the glass surface. Long tubular carbon nanotube imparts the required roughness to the system whereas the hydrophobic polyamine controlled the surface energy of the film (Hsu *et al.*, 2013). Recently, Guo *et al* have shown the formation of the superhydrophobic surface which shows an interesting rapid self-healing capability, a much required proper for the robust and rugged application. As-prepared dopaminesilica trimethylsilyl modified gel powder was dispersed in ethanol and gets coated over different substrates including cotton, paper, wire mesh, foam, wood, metal, sponge (Si *et al.*, 2015). Considering the low cost and non-toxicity of TiO_2 nanoparticles, a bunch of reports exist where these nanoparticles were used to design superhydrophobic surfaces (Xu *et al.*, 2009; Milanesi *et al.*, 2010; Tomovska *et al.*, 2011; Xu *et al.*, 2013). This is elaborately discussed in recent review article by Jiang *et al* (Liu *et al.*, 2014). Parkin and coworkers have shown the formation of TiO_2 based superhydrophobic surface that functions both in air-solid and oil- solid interface equally. Chemically modified these TiO_2 nanoparticle were coated over various soft and hard substrates and demonstrated for droplet bouncing experiments (Figure 1.18) (Lu *et al.*, 2015). Here, to enhance the robustness as well as the longevity of the superhydrophobic coating, adhesive materials are introduced which did not change the water repellent nature of the coatings. Recently, robust superhydrophobic coating material was developed by Zhou and coworkers in ambient condition that consist of additional binder triethoxysilyl-terminated fluoropolysiloxane (FPU), polymethylphenyl-siloxane (PMPS), and 3-aminopropyltriethoxysilane. These enhance the mechanical properties and resistance of the material towards organic contaminants (Zhou *et al.*, 2013). Similar sol-gel process was adapted to prepare trimethylsiloxane (TMS) modified SiO_2 nanoparticles that provide a robust and antireflective superhydrophobic film. Here, authors have also demonstrated the durability of the coated film which retained its water repelling and self-cleaning properties even after exposing the surface outside for 2000 h (Manca *et al.*, 2009). Huang and Lin have reported the formation transparent superhydrophobic film where the coating material was synthesized with 1H,1H,2H,2H

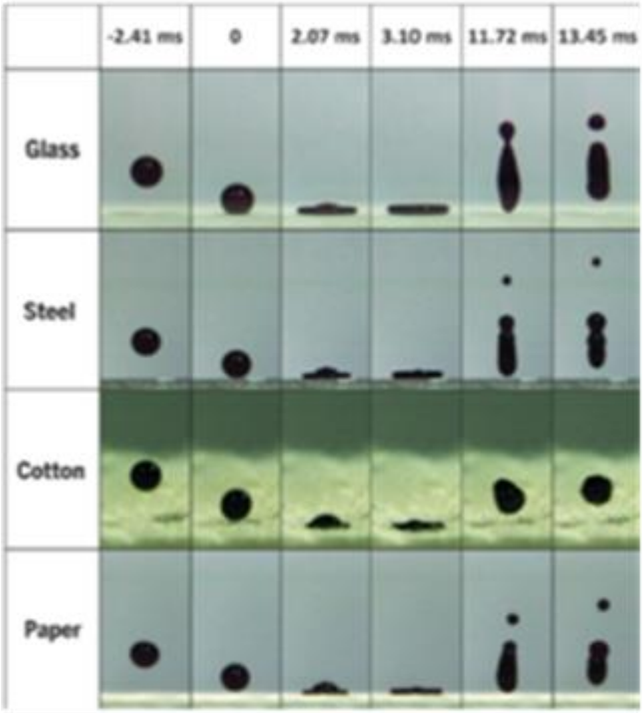


Figure 1.18 Time resolved photographs of bouncing of water droplets on the coated glass, steel, cotton wool, and filter paper surfaces. Reproduced with permission from (Lu *et al.*, 2015) © 2015 AAAS

perfluoro-octyltrichlorosilane at 80 °C (Huang and Lin, 2014). Similar to these, several other reports from various research groups have demonstrated the fabrication of superhydrophobic surfaces where sol-gel process was used predominantly.

1.5.2.2 Self-Assembly Assisted Non-Wettability

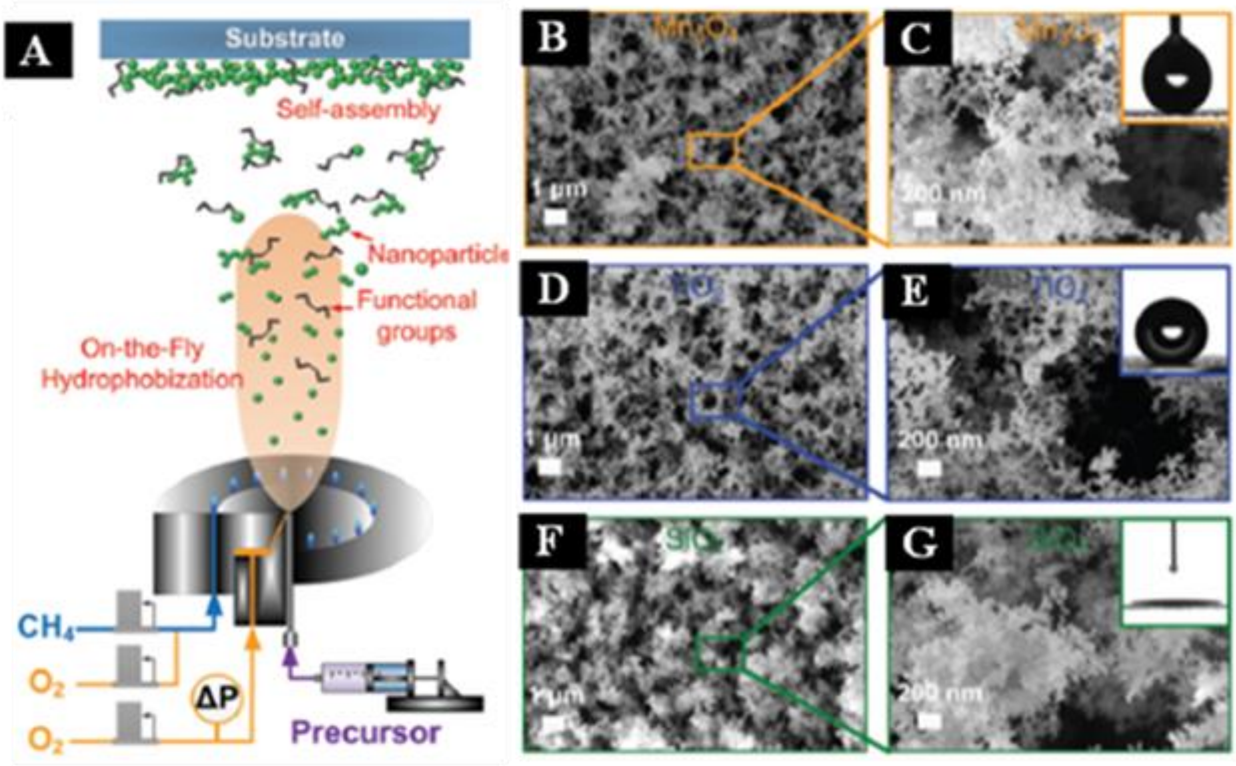


Figure 1.19 (A) Schematic diagram for the synthesis of ultraporous superhydrophobic nano-layers. SEM images of different nano-layers made of (B,C) Mn_3O_4, (D,E) TiO_2 and (F,G) SiO_2. Reproduced with permission from (Liu *et al.*, 2016) © 2016 Royal Society of Chemistry.

Self-assembly, being a great way to import the collective molecular features in the materials, several approaches have been made to fabricate superhydrophobic surfaces (Li *et al.*, 2014; Yang *et al.*, 2014; Sun *et al.*, 2015; Leem *et al.*, 2016; Liu *et al.*, 2016; Roy *et al.*, 2016). One of the important aspects of self-assembly is that it is a spontaneous process that forms an ordered ensemble of molecules. Such ordered assembly can promote the formation of nanostructures which is much essential for superhydrophobicity (Whitesides and Boncheva, 2002). Lu *et al.* have reported self-assembled reduced graphene-based superhydrophobic foam that separates oil or organic solvent efficiently from water. Cost-effective thermal reduction processed superhydrophobic material was prepared melamine foam which incorporates various important characteristics like thermal and mechanical stability along with high porosity (Zhu *et al.*, 2015). Similarly, Xin *et al*. have constructed hierarchical two-layer self-assembled structured graphene and TiO_2 nanofilm over different structures. This material showed excellent superhydrophobicity along with stimuli-responsive characteristics like directional movement of water and controlled wettability. It was guided by UV sensitive conversion of TiO_2 to hydrophilic state (Liu *et al.*, 2015). Formation of ultraporous superhydrophobic surface through a one-step solvent-free process is demonstrated by Tricoli and coworkers (Liu *et al.*, 2016). Mn_3O_4, ZnO, SiO_2 and TiO_2 nanoparticle aerosols mediated developed surfaces showed Cassie-Baxter dewetting state. Figure 1.19A schematically represent the fabrication these ultraporous superhydrophobic surfaces. SEM images of (B,C) Mn_3O_4, (D,E) TiO_2 and (F,G) SiO_2 deposited surface and their corresponding water contact angle.

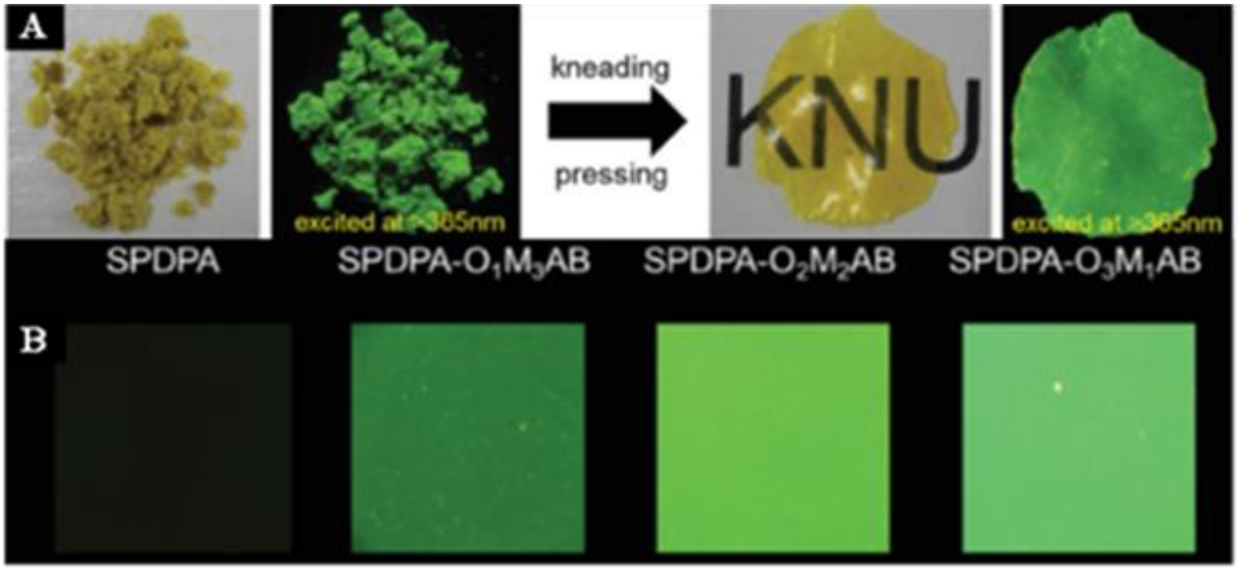


Figure 1.20 (A) Bulk solid before and after kneading and pressing process. (B) SPDPA and SPDPA-O_xM_yAB complex films. Reproduced with permission from (Jin *et al.*, 2016) © 2016 John Wiley and Sons.

Such self-assembled molecular structures not only import water repelling property to the surfaces, this can also exhibit anti-frosting application depending on the characteristics of incorporated low surface energy molecules (Kim *et al.*, 2015). In addition, these multi-layered self-assembled structures have proven to be an excellent route to design durable water repellent surfaces (Van *et* *al.*, 2013). Shiratori *et al* demonstrate the fabrication of multiscale, layered material that shows excellent water repelling property. Such layer structures were obtained through the layer by layer deposition of negatively charged poly(acrylic acid) (PAA) and positively charged TiO_2 nanoparticles over nanofiber membrane. This was further functionalised with fluroalkyl silane to introduce the superhydrophobic property (Tasuku *et al.*, 2007). Apart from these, liquid-liquid interfacial self-assembly technique was adopted by Zhang *et al*. to design 2D-petal like hybrid composite through an electrostatic interaction between two functional groups, amine and carboxyl from octadecylamine and of nikel dopped CdS quantum dot surface (Zhang *et al.*, 2013). Fluorescent hydrophobicity material was introduced through the electrostatic self-assembly of sulfonated poly(diphenylacetylene) $(octadecyl)_x(methyl)_y$ ammonium bromide complexes. Author have proposed the use of such material in FL image writing, fingerprinting, stamping, and inkjet printing (Jin *et al.*, 2016). Photograph of bulk SPDPA–O_3M_1AB complex before and after pressing in normal light and UV light presented in Figure 1.20A. Figure 1.20B shows various SPDPA-O_xM_yAB complex coated films under UV light.

1.5.2.3 Layer Structured Non-Wettable Surfaces

In general, multi-layer superhydrophobic surfaces have shown a diverse application potential in different fields because of their enhanced stability as well as durability (Yonghao *et al.*, 2010; Shirtcliffe *et al.*, 2011; Verho *et al.*, 2011). Due to these layered structures, even if a few uppermost layers of the surface got damaged, underneath layers retain functional and keep the surface properties intact. Such layered structured superhydrophobic surface was introduced using SiO_2 nanoparticle where the number of the layers were seen to control the wetting characteristics of the films. In this case, the layered structured surface was made through the interaction of charged species, namely positively charged ionic liquid and negatively charged silica particles (Zhang *et al.*, 2014). Recently, Zhu *et al*. have introduced graphene oxide/TiO_2 based hybrid superhydrophobic film through a layer by layer construction process (Sun *et al.*, 2012). Such an ultra-thin surface was observed to switch its wettability upon UV stimuli. Along with a layer by layer deposition of polydiallyldimethylammonium chloride and silica particles, chemical vapour deposition of perfluorooctyltriethoxysilane was used by Yang and Deng to demonstrate the water repelling characteristics of hydrophilic paper. Here the surface was shown to maintain its mechanical property even after prolong immersion inside the water (Yang and Deng, 2008).

Similar methodology was adopted by Zhao *et al*. where UV irradiation was introduced to make the cross-linking between the azido-functionalized silica nanoparticles and poly(allylamine hydrochloride) as well as between the coating and substrate. While this cross-linking enhanced the durability of the material, water-repelling property of the material was introduced by tridecafluorooctyl triethoxysilane treatment which essentially provided the chemically durability towards acid solutions and various organic solvents (Zhao *et al.*, 2012).

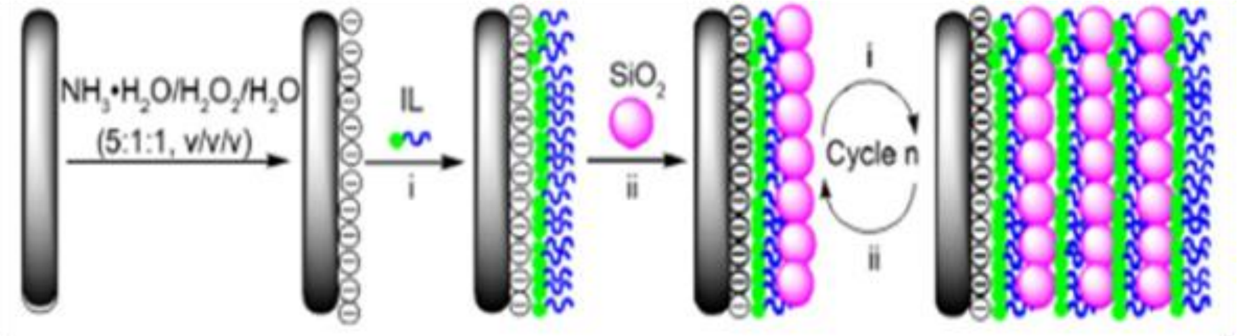


Figure 1.21 Schematic representation of the process that leads to a multi-layered superhydrophobic surface. Reprinted with permission from (Zhang *et al.*, 2014) © 2014 Elsevier.

Layer-by-layer deposition of positively charged 1-dodecyl-3-methylimidazoliumbromide and negatively charged SiO_2 nanoparticles were used by Zhang *et al* to prepare a superhydrophobic film over a glass surface. While the SiO_2 nanoparticles control the roughness in the surface, incorporation of ionic liquid (IL) layers decreases the surface energy (Zhang *et al.*, 2014) and results in a water contact angle greater than 150°. Figure 1.21 schematically represents the fabrication of layered structured superhydrophobic surface. Similar to these, layer by layer self-assembly of materials or molecules over cellulosic surfaces can also lead to the formation of superhydrophobic surfaces (Peng *et al.*, 2016). For instance, Zimmermann and coworker have developed nanofilament structures over textile surfaces that showed excellent wear resistance upon various mechanical tests (Zimmermann *et al.*, 2008). Surprisingly, the surface was observed to maintain its water repelling property with equal efficiency in spite of the fragile nature of the nanostructures. SEM images of silicone nanofilament coated fibers are shown in Figure 1.22. Recently, Bhushan and coworkers have developed a layered structured superoleophobic surface for efficient water oil separation (Brown and Bhushan, 2015). In this case, layered assembly of the materials, polyelectrolyte binder, SiO_2 nanoparticles, and fluorosurfactant, was controlled through the electrostatic interaction of the charged molecules. Figure 1.23 shows the schematic representation of the layers. Durability of the transparent coating was studied in details through different micro and macro wear experiments.

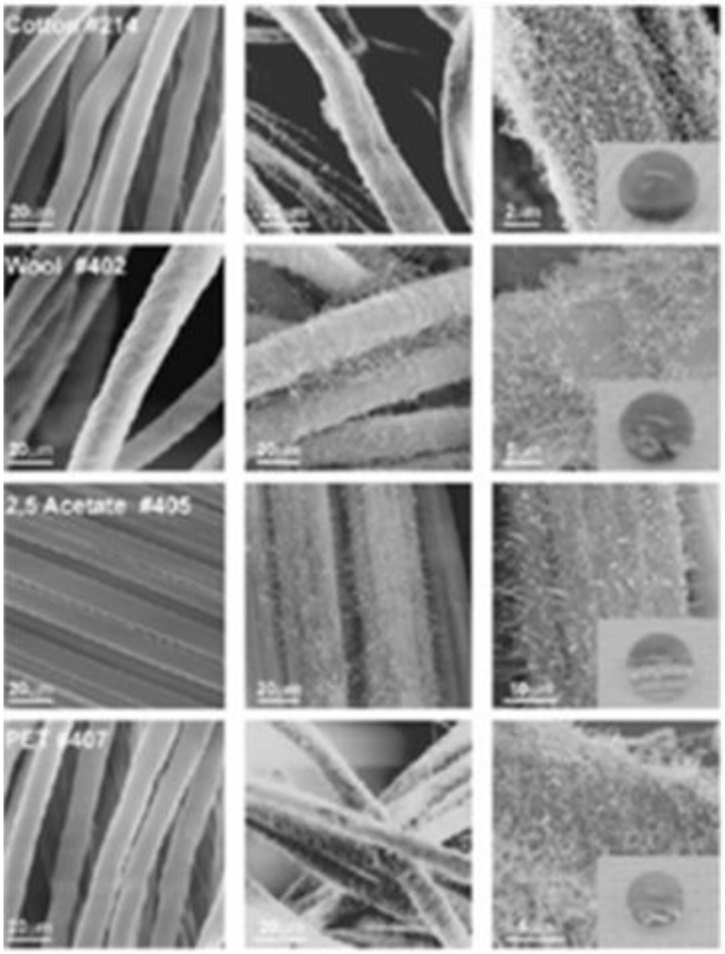


Figure 1.22 SEM images of uncoated (left) and coated (middle and right) textile fabrics in different magnifications. Insets, water drop on the respective coated fabrics. Reproduced with permission from (Zimmermann *et al.*, 2008) © 2008 John Wiley and Sons

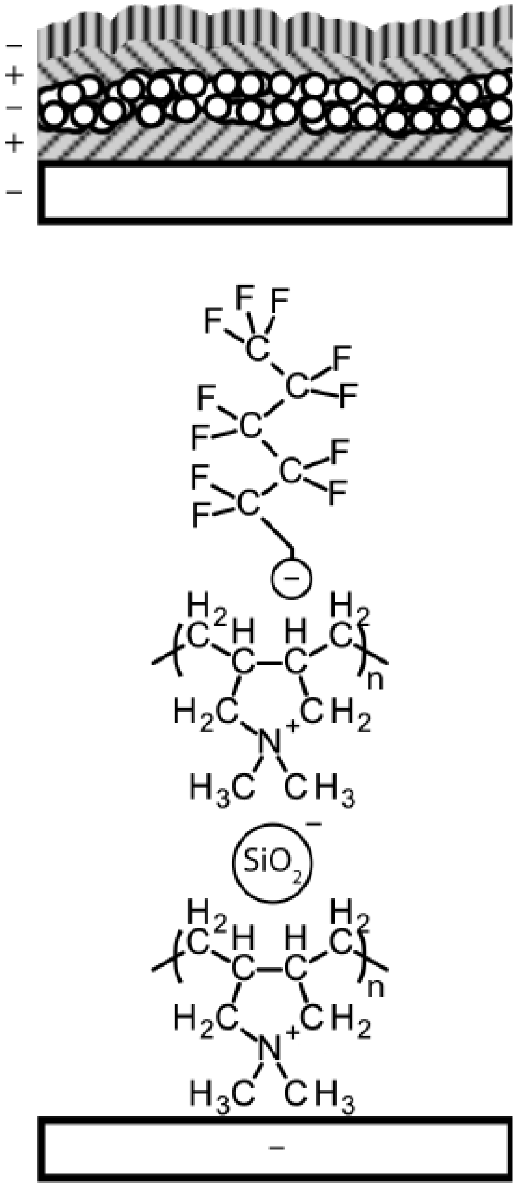


Figure 1.23 Schematic of layer-by-layer composite coating. Reprinted with permission from (Brown and Bhushan, 2015) © 2015 Springer Nature.

1.5.2.4 Chemical Deposition Directed Non-Wettable Surface

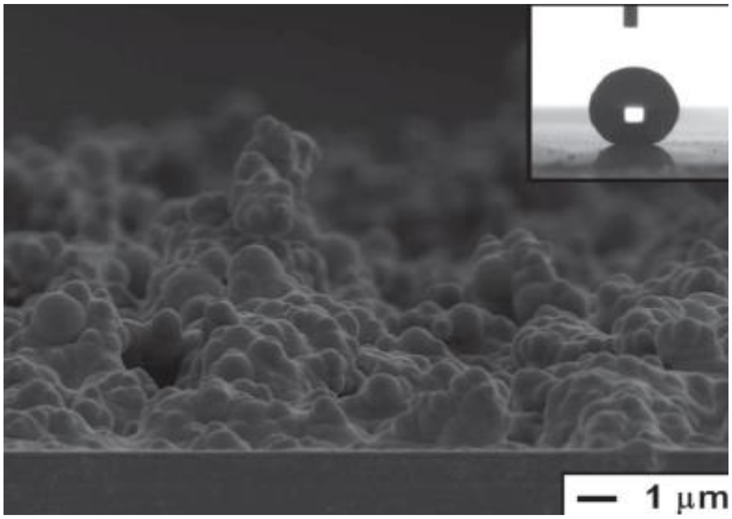


Figure 1.24 SEM image of TiO2 embedded polymer film. Inset, water drop sitting over the surface. Reproduced with permission from (Crick *et al.*, 2012) © 2012 John Wiley and Sons.

In order to fabricate superhydrophobic surfaces, different kind of chemical deposition techniques have been introduced by various research groups. Depending on the deposition conditions, these are mostly categorized in chemical bath deposition (CBD), chemical vapor deposition (CVD) and physical vapor deposition (PVD), and electrochemical deposition. One of the important aspects of these methodologies includes the formation of aligned nanostructures over suitable substrates. CVD process consists of gas-phase growth of materials over a solid matrix/ substrate through a surface reaction. Development of various patterned structures, honeycomb, island, post, *etc.* followed by the modification through CVD process to obtain liquid repelling property are well known in this context (Hozumi and Takai, 1997; Li *et al.*, 2002; Sun *et al.*, 2003; Zhu *et al.*, 2005; Tavana *et al.*, 2006; Du and He, 2011). Pourabbas *et al*. and Parkin *et al*. have demonstrated a one-step CVD and aerosol assisted chemical vapor deposition method (AACVD) to prepare superhydrophobic surfaces (Crick *et al.*, 2012; Rezaei *et al.*, 2014). Figure 1.24 shows the SEM image of TiO_2 nanoparticle embedded polymer film. Water contact angle over this surface is pictorially represented in the inset. Prawer *et al*. have reported the growth of aligned carbon nanotubes on Fe-N coated Si substrate through a CVD process. To introduce the superhydrophobic property, CNT surface was modified with zinc oxide film and low surface energy molecules (Huang *et al.*, 2005). Apart from these, use of chemical bath deposition technique to fabricate superhydrophobic surface (Wu *et al.*, 2005) is reported by Zhou *et al*. Well-defined sharp nanopin structured this surface was made with $CoCl_2$ and NH_2CO in water. Later this was treated with lauric acid and demonstrated for excellent superhydrophobicity (water contact angle 178°) (Hosono *et al.*, 2005). SEM and TEM images of these nanopin structures are presented in Figure 1.25. Figure 1.25D represent the simple model of the surfaces.

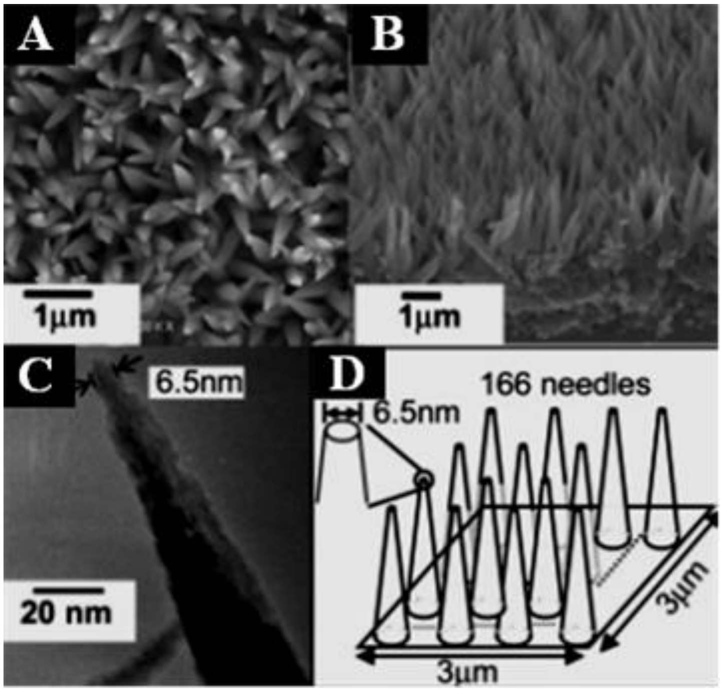


Figure 1.25 FESEM (A,B) and TEM (C) images of nanopin structures prepared through CBD method. (D) Schematic representation of the surface. Reproduced with permission from (Hosono *et al.*, 2005) © 2005, American Chemical Society

In the context of fabrication of liquid repelling surfaces, electrodeposition technique has also proven its wide applicability because of it easy one-step procedure which is not restricted to the size of the substrates (Shi *et al.*, 2005; Shi *et al.*, 2007; Wolfs *et al.*, 2014). Jiang *et al*. have used various conductiong surface including copper, iron, zinc, and aluminium to demonstrate the superhydrophobicity developed through this process (Xi *et al.*, 2008). Electroless galvanic deposition processed fabrication of an extreme superhydrophobic surface was shown by Saunders and coworkers. Here, in the first step, a clean copper or zinc surface was dipped inside a silver nitate solution and finally coated with low surface energy molecule, heptadecafluoro-1-decanethiol through a solvent immersion process (Larmour *et al.*, 2007). Authors also showed the mirror-like appearance of the coated surface when it was dipped inside the water and viewed from a particular angle (Figure 1.26 A,B). This was attributed to the trapped air layer over the surface. SEM images of the coated surface showed sufficient roughness (Figure 1.26C) to demonstrate the Cassie-Baxter state. Water droplet over this modified copper surface showed a contact angle greater than 170° (Figure 1.26D). With this excellent surperhydrophobic surface, authors have developed a model of pond skaters (Gerridae) having a weight of 0.13 gm and presented in Figure 1.26E.

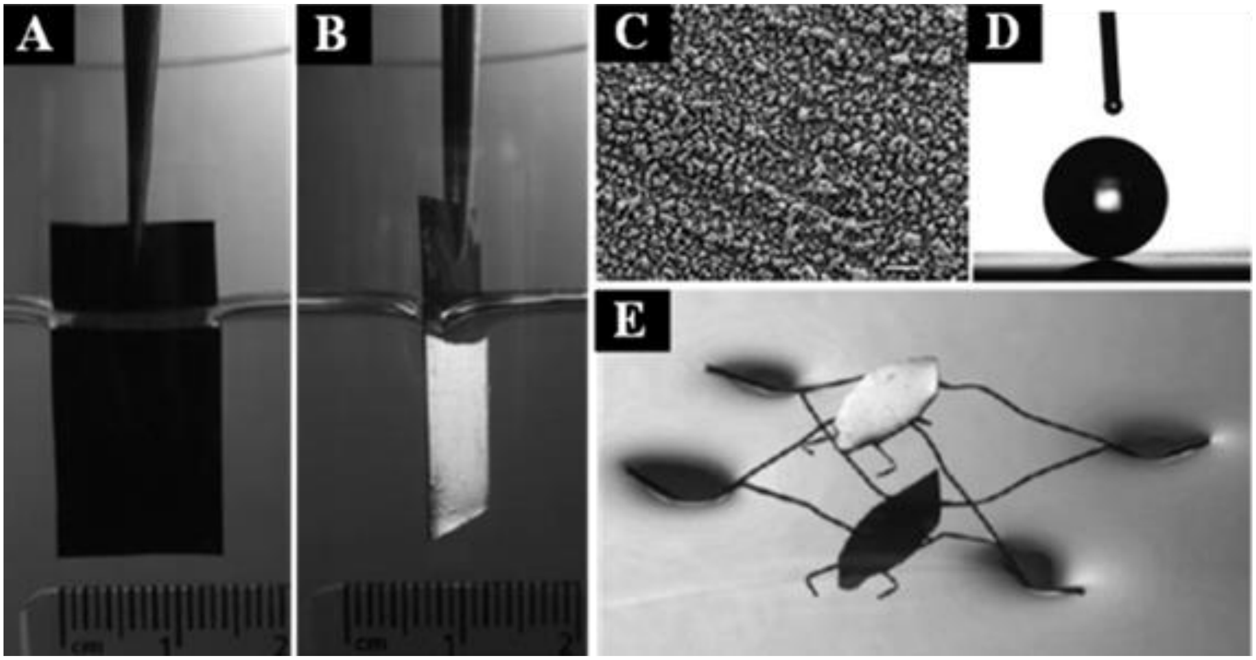


Figure 1.26 (A,B) Superhydrophobic copper plate in water. (C) SEM image of the rough surface (silver on copper). (D) Water contact angle. (E) A metallic model "pond skater" standing on a water surface. Reproduced with permission from (Larmour *et al.*, 2007) © 2007 John Wiley and Sons.

1.5.2.5 Electrospun Fiber Based Non-Wettable Surface

Electrospinning is a great tool to develop fibrous structures having nanometer to micrometre dimensions. Because of such dimensional diversity, it also imposes required roughness which is essential to fabricate superhydrophobic surfaces. People have used both this method alone (Acatay *et al.*, 2004; Ma *et al.*, 2005) and a combined method (electrospinning along with other methods) for the fabrication of superhydrophobic surfaces (Ma *et al.*, 2005). For example, Kim and coworkers have fabricated polycaprolactone (PCL) based superhydrophobic surface having nanopores and microscale pyramidal structures (Yoon *et al.*, 2010). TiO_2 nanoparticle incorporated polystyrene (PS) and polyvinyl chloride (PVC) fibers (Figure 1.27) were made by Nuraje *et al* that showed excellent water repellency (Asmatulu *et al.*, 2011). To control the low surface energy of the fiber surface, often fluorin-containing polymers are used, though such polymers are expensive. For example, poly[bis(2,2,2-trifluoroethoxy)phosphazene] based superhydrophobic material was prepared by Allcock *et al* where water contact angle was 150° (Singh *et al.*, 2005). Poly (vinylidene fluoride) (PVDF) based superhydro-phobic membrane was synthesized by Zhu *et al*. In this case, authors have shown the water contact angle over these polymer fibers can be in maximized to 171° with a loading of 8 wt% ZnO nanoparticles (Liu *et al.*, 2016). Figure 1.28 shows the SEM images of PVDF membrane having different wt% of ZnO. Effect of 1H,1H,2H,2H-perfluorodecyltriethoxysilane (POTS) and ammonia on the wettability of the surface are shown in the Figure 1.28. Here, these reagents (for POTS v/v=1./100 and ammonia v/v= 1/50, respectively) were directly mixed with the polymer solutions.

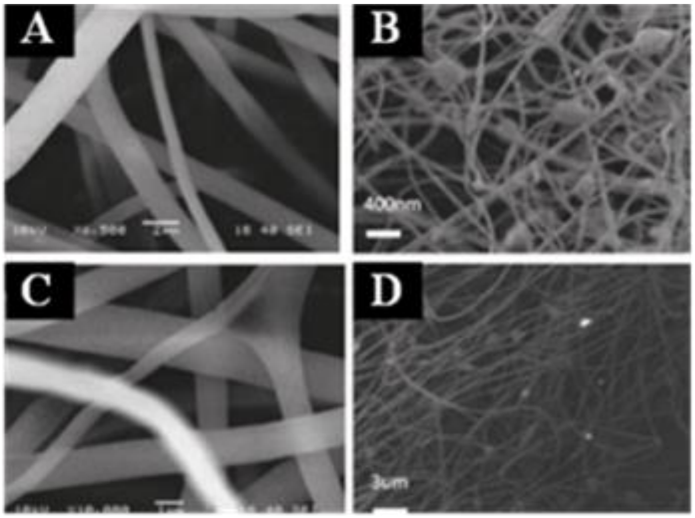


Figure1.27 SEM images of PVC (A,B) and PS (C,D) fibers having different diameters. Reproduced with permission from (Asmatulu *et al.*, 2011) © 2011, American Chemical Society

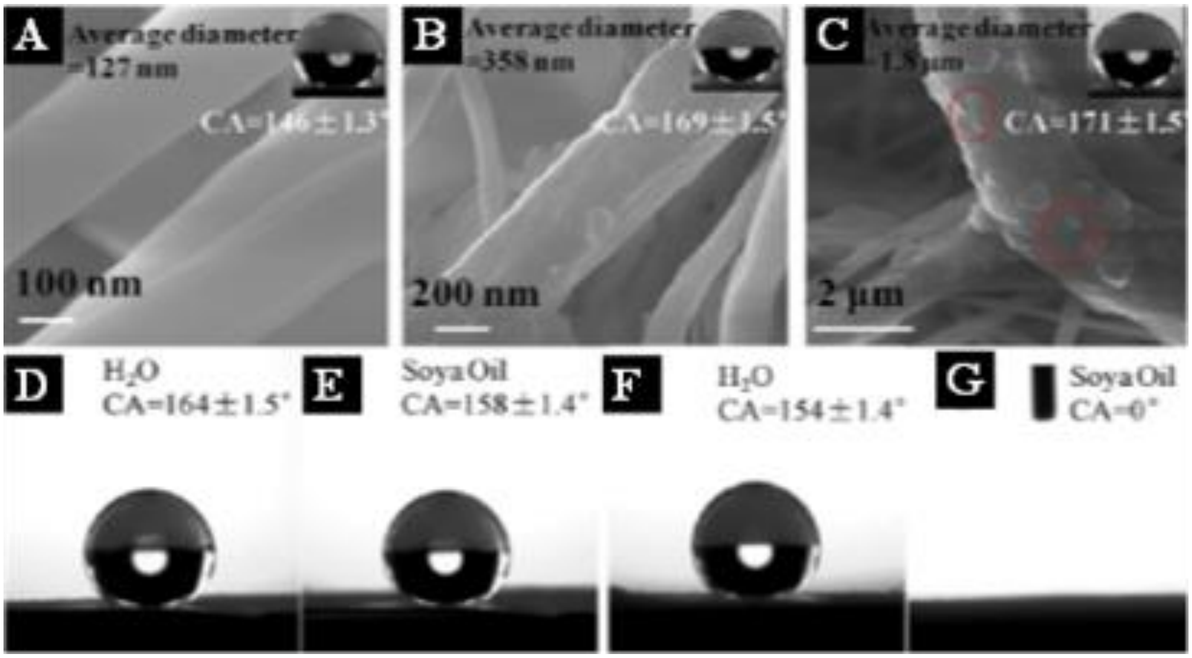


Figure1.28 SEM images of pure PVDF membrane (A) and ZnO incorporated PVDF membrane. (B) PVDF/5 wt.% ZnO (C) PVDF/10 wt.% ZnO. Wettability of the membrane upon adding POTS (D-F) and ammonia (G). Reprinted with permission from (Liu *et al.*, 2016) © 2016 Elsevier

1.6 Polymer Based Liquid Repellent Surface

Designing superhydrophobic or superoleophobic materials from synthetic polymers have become one of the immensely pursued research topic in this area. Easy coating of these materials through spray coating, spin coating and others added an extra value to this (Cao *et al.*, 2009; Wu *et al.*, 2009). Several of such polymer-based materials have been commercialized in the last few years. In general, these composite materials are made in an appropriate solvent system with dispersed polymeric binders having various micro/ nanoparticles (Steele *et al.*, 2009; Schutzius *et al.*, 2011).

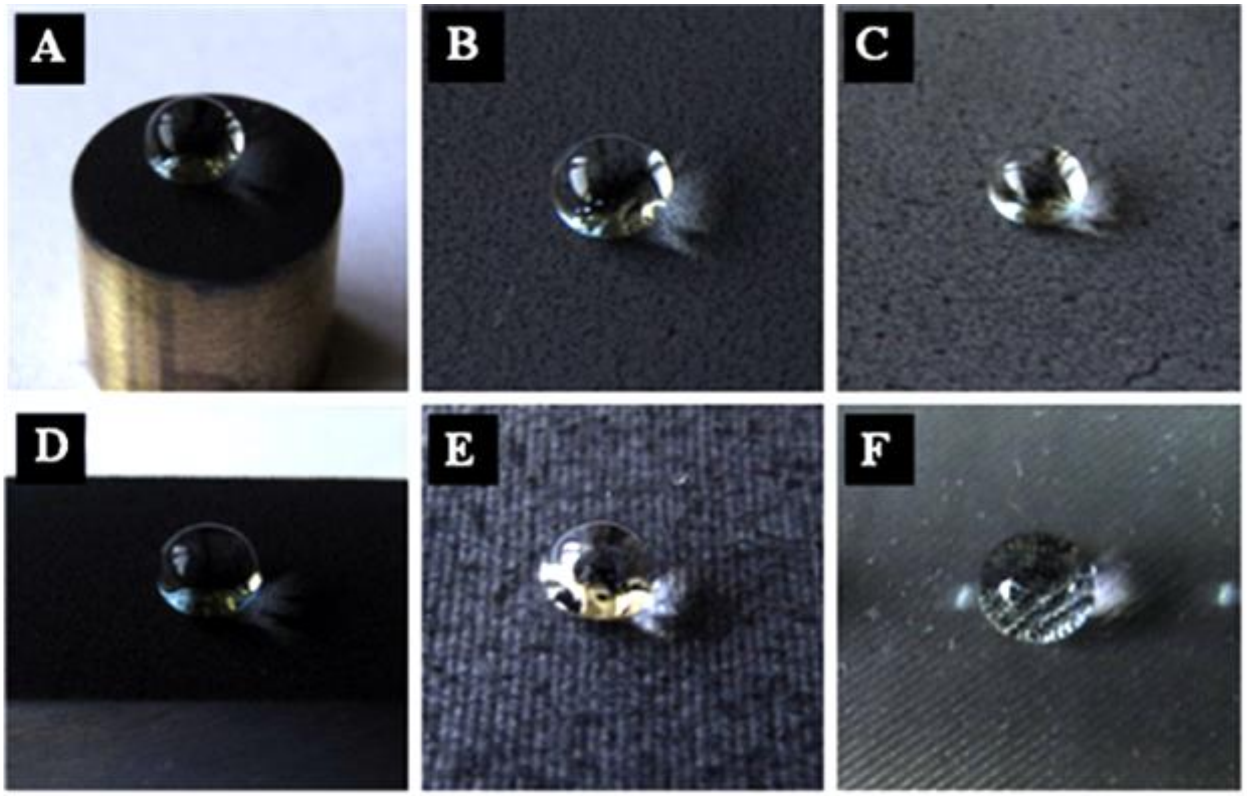


Figure 1.29 Water droplet on coated (A) copper pillar, (B) glass plate, (C) paper, (D) stainless steel, (E) fabric, and (F) copper mesh. Reprinted with permission from (Tang *et al.*, 2014) © 2014 Elsevier.

Polyurethanes, fluorinated acrylics, polyvinylidene fluoride, styrene copolymers, PVDF, polydimethylsiloxane (PDMS), and poly(tetrafluoroethylene) (PTFE) are frequently used in this purpose. For instance, Li and coworkers have fabricated MoS_2 based superhydrophobic nanocomposite with polyurethane matrix that showed excellent durability and wear resistance property against abrasions (Tang *et al.*, 2014). Figure 1.29 shows the images of water droplet over various substrates coated with as-prepared material. To incorporate an additional property in the superhydrophobic film, Athanassiou *et al* have introduced graphite-PTFE polymer composite and coated over different solid surfaces like glass, ceramics, and metals. While the polymeric component of the material helped to achieve the nonwettability, colloidal graphite controlled the electrical conductivity and high temperature resistance capacity of the film (Bayer *et al.*, 2012). Surface roughness of the coated film was measured through the AFM study (Figure 1.30A,B). Figure 1.30C shows the composite material coated glass slide where water contact angle was found to be 167°. Kapton film coated with superhydrophobic material is presented in the Figure 1.30D. Importance of such materials are easily observable in various applications including heat exchanger, flexible electronics, energy conversion where both the thermal and electrical conductivity are highly required.

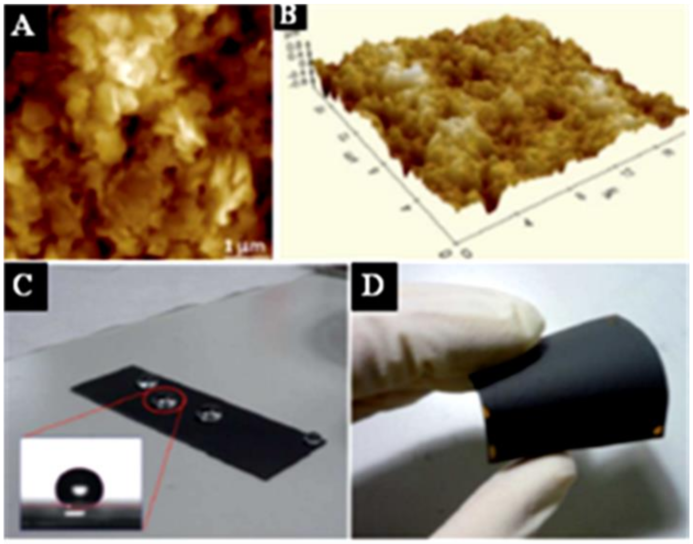


Figure1.30 (A,B) AFM images of a superhydro-phobic film.(C) Water droplet over a coated glass slide. (D) Photograph of material coated Kapton film. Reproduced with permission from (Bayer *et al.*, 2012) © 2012 Royal Society of Chemistry.

Being inert towards various chemical environment, several reports on siloxane based superhydrophobic materials are exist in literature (Bayer *et al.*, 2010; Jeong *et al.*, 2012). Recently, Jia *et al* have developed PDMS based superhydrophobic material and demonstrated an important self-healing property which is crucial for several applications (Xue *et al.*, 2014). In order to get the mechanically durable superhydrophobic surface, Bayer and coworkers have developed fluorinated polymer-clay composite that shows excellent stability upon multiple sandpaper abrasion (Ilker *et al.*, 2009). To show the effect of such external perturbations, coated surface was studied in detail with static contact angle and contact angle hysteresis. Similar mechanically stable surface with additional drag reduced feature has been developed with carbon nanotube-based polymer composite. SEM images of the nano and hierarchical structured surface are presented in

Figure 1.31. Uniformly distributed sprayed carbon nanotubes in the epoxy matrix not only provides the long-term stability of the surface towards water pressure, it kept the surface functioning even after multiple wear resistance experiments (Jung and Bhushan, 2009). Except these, several biopolymer based liquid repelling surfaces are also known which are robust and can be made in large scale (Bayer *et al.*, 2009; Milionis *et al.*, 2014; Milionis *et al.*, 2015).

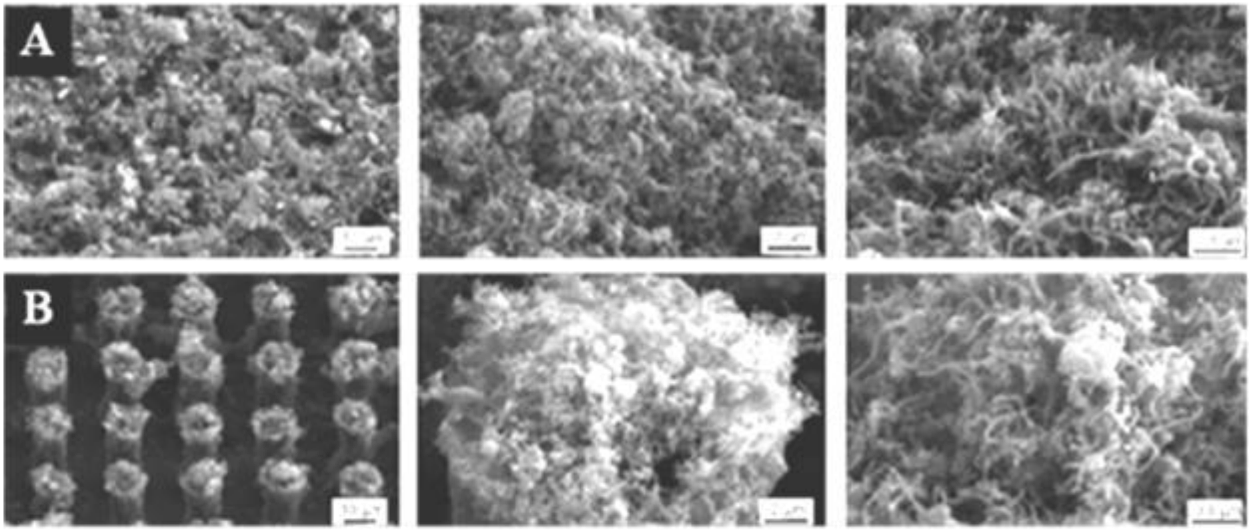


Figure 1.31 SEM images of nano (A) and hierarchical (B) structures fabricated with CNTs (after treating at 120 °C for 3 h). Reproduced with permission from (Jung and Bhushan, 2009) © 2009, American Chemical Society.

1.7 Use of Cellulosic Materials to Fabricate Superhydrophobic Surfaces

Considering the availability and cost of various biopolymers, cellulosic materials have shown a significant input in the domain of liquid repelling surfaces, although it is known as a hydrophilic and water absorbing material. From the chemistry point of view, such inherent water absorbing property of cellulosic materials comes from their surface hydroxyl groups. However, the presence of these functional groups enhance the possibility of chemical modification. Recent advancement on the development of liquid repelling surfaces using various cellulosic materials is consolidated by Kuusipalo and coworker in their review article (Teisala *et al.*, 2014). In most of the cases surface of the cellulosic materials get modified with functionalized nanomaterials (Gao *et al.*, 2009; Duan *et al.*, 2011). For example, Lin *et al* have reported the preparation of water repelling textile and paper substrates with functionalized SiO_2 nanoparticles. Here, the hydrolysis of two different silane precursors lead to the formation nanoparticle which can be coated by different coating techniques like dip coating, spray coating and spin coating (Wang *et al.*, 2008). Water drops over a coated surface possesses a stable contact angle of 170° (Figure 1.32A). SEM image and corresponding elemental mapping of the material coated polyester fibers are shown in Figure 1.32B-G. Even cellulose nanofibers made filter paper was made highly water repellent through a subsequent deposition of calcium carbonate and alkyl ketene dimer. Here the coating of calcium carbonate over the cellulosic surface helped to enhance the roughness of material (Arbatan *et al.*, 2012).

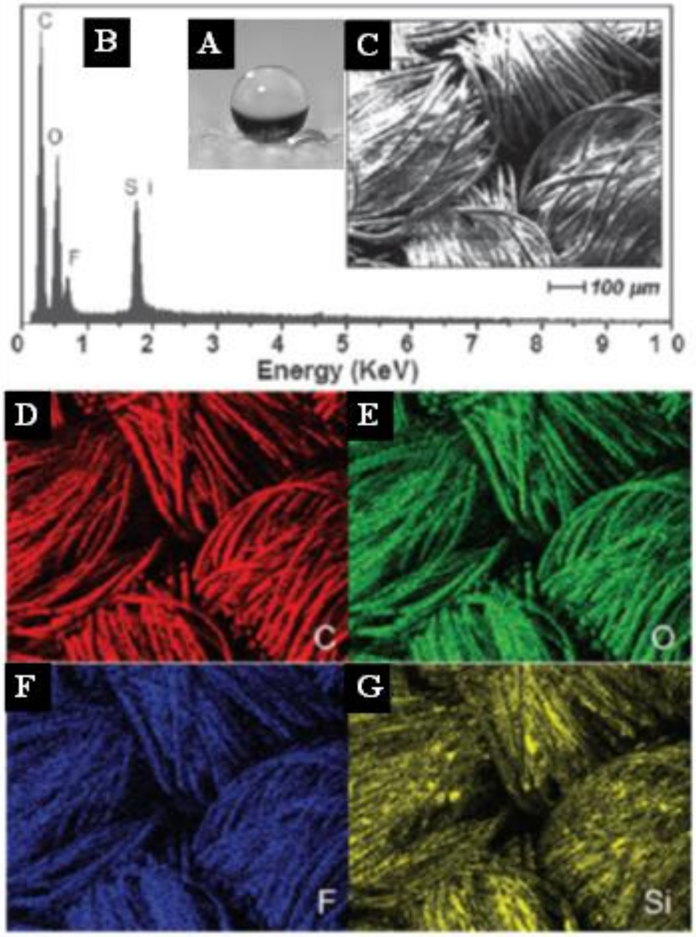


Figure1.32 (A) Water drop on superhydrophobic surface.(B) EDAX spectrum. (C) SEM image and (D-G) corresponding element-al mapping. Reproduced with permission from (Wang *et al.*, 2008) © 2008 Royal Society of Chemistry.

Use of different low surface energy polymers in the context of importing superhydrophobicity in the cellulosic material also has explored intensely (Bayer *et al.*, 2011; Zhou *et al.*, 2012). For example, PDMS modified SiO_2 nanoparticles and PS were used by Lu *et al* to obtain robust superhydrophobic- superoleophilic material for the selective absorption oil. Such oil absorbing property of the material was demonstrated with different non-polar hydrocarbons as well as diesel oil. (Wang *et al.*, 2010). To enhance the oil absorbing capability of the hydrophobic substrates, Yang *et al*. impregnated epoxy based coating over a paper that shows high water contact angle of 152° and hexadecane contact angle 0°. However, the surface showed sticky characteristics similar to the rose petal effect (Huang *et al.*, 2012). Recently, Lin and coworkers have fabricated superamphiphobic fabrics through a dip coating of polymeric solution (Figure 1.33). Contact angle of water droplet and hexadecane droplet over the substrates was seen to be greater than 170° and 155°, respectively (Figure 1.33B). Author also have demonstrated the durability of the material with different abrasion tests as well as other relevant experiments including exposed to acidic and basic conditions and ozone treatment (Zhou *et al.*, 2013). Similar to this, spray coating is also known as a frequently used method to impart superhydrophobicity in cellulosic materials. In this case, dispersed solutions are developed in various organic solvents and get coated over the surface of interest. In this context, several reports exist in the literature (Lin *et al.*, 2006; Barona and Amirfazli, 2011; Bayer *et al.*, 2011). For instance, recently Saji *et al*. have demonstrated the formation of transparent water repelling coating with surface modified SiO_2 nanoparticles where the wettability of coated surface dependent on the dispersing medium which basically controls the extent of aggregation of the modified nanoparticles (Ogihara *et al.*, 2012).

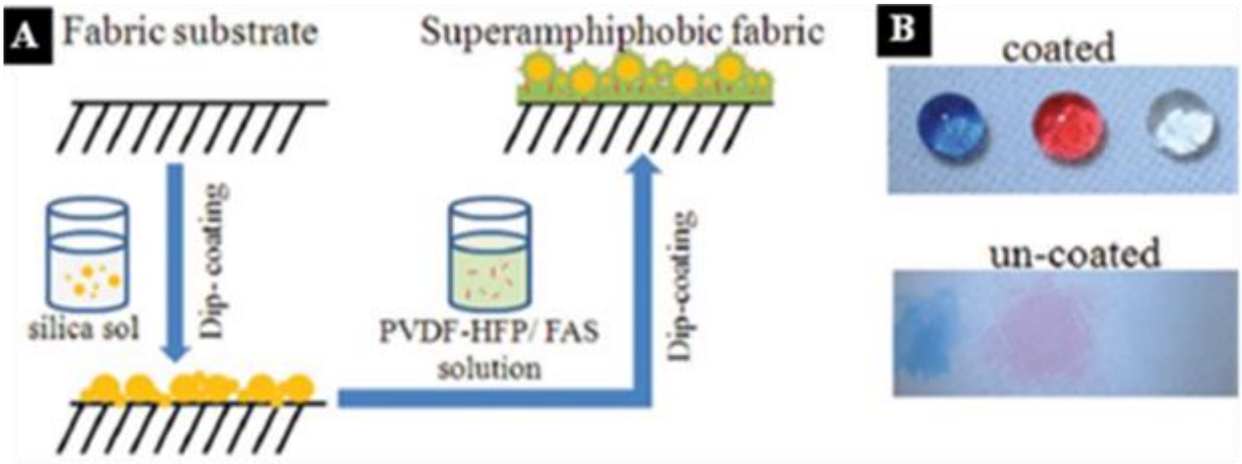


Figure 1.33 (A) Schematic representation towards the fabrication of superamphiphobic fabrics. (B) Liquid drops (blue-colored water, red-colored hexadecane and clear soybean oil) over coated and uncoated fabrics. Reproduced with permission from (Zhou *et al.*, 2013) © 2013 John Wiley and Sons.

Apart from these, several other approaches also have been made particularly when fabrication of cellulosic material-based superhydrophobic surfaces are concerned. For example, formation of water repellent surface through polymerization, in situ grown morphologically different particles, plasma processing, laser deposition technique, solvo-thermal process *etc.* are well known (Balu *et al.*, 2008; Georgakilas *et al.*, 2008; Balu *et al.*, 2009; Zhang *et al.*, 2011). Recently, Fan *et al* have reported the formation of fluoropolymer coated robust superhydrophobic cotton where water drops sit at a contact angle of 160°. Durability of the surface was demonstrated with laundering test. Even after extensive washing in laundering machine, surface was seen to remain functioning and retained its water repelling property intact. Here, the polymerization of 1H,1H,2H,2H nonafluorohexyl-1-acrylate was performed through a radical mechanism where the radical was generated by a x-ray radiation. (Deng *et al.*, 2010). Magnetic field induced development of superhydrophobic surface was described by Lin *et al*. Surface-functionalized magnetic nanoparticle was deposited over various cellulosic material under the magnetic field that provides enhanced hierarchical structures having a water contact angle greater than 160 (Fang *et al.*, 2010).

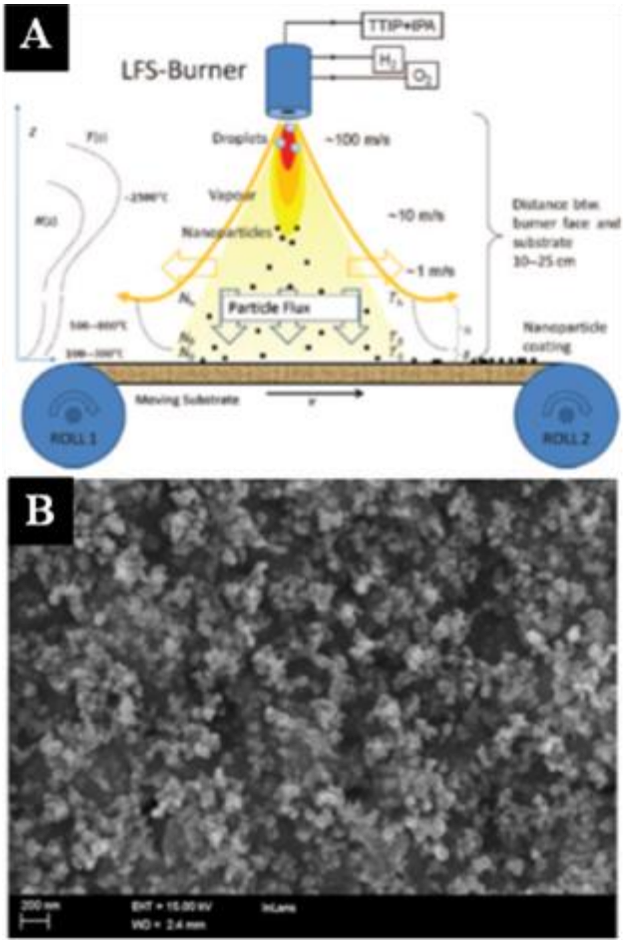


Figure1.34 (A) Schematic of the LFS-coating. (B) SEM images of coated paperboard. Reprinted by permission from (Mäkelä *et al.*, 2011) © 2011 Taylor & Francis.

Fabrication of superhydrophobic-superoleophobic material from porous, network structured, solid nanocellulose matrix was shown by Ras *et al*. (Jin *et al.*, 2011). Nanocellulose based aerogel was treated with FOTS through CVD techniques and observed to show water and oil repelling characteristic having a contact angle of 160° and 153° (for paraffin oil), respectively. Interestingly, surface was seen to maintain the plastron layer (trapped air on the structured surface) both inside oil and water even after one weak. However, in any of the cases, liquid droplets were not seen to roll off even after the surface was made upside down. Later on, potential use of such porous hydrophobic material in the domain efficient oil-water separation was demonstrated by Cervin and coworkers (Cervin *et al.*, 2012). In the context of porous material, Xiao *et al* have produced porous powder-like material of polydivinylbenzene (PDVB) which provides high transparency and excellent superhydrophobic property once it is painted over the substrates. Recently, several research groups have demonstrated the development of transparent, nonwettable TiO_2 coatings over cellulosic materials (Teisala *et al.*, 2010; Mäkelä *et al.*, 2011; Stepien *et al.*, 2011; Aromaa *et al.*, 2012; Stepien *et al.*, 2012; Teisala *et al.*, 2012; Stepien *et al.*, 2013). Here, the coating was done through a liquid flame spray technique (LFS) where liquid titanium precursor forms fine nanoparticles due to the presence of high-temperature oxygen-hydrogen flame and directly gets deposited over the surface. Non-wetting property of these rough TiO_2 nanoparticle coated surfaces originate through the accumulation of various hydrocarbons that forms in hot spray environment. Figure 1.34A schematically illustrate the LFS coating procedure (Mäkelä *et al.*, 2011). SEM image of the microstructures developed over paper board is presented in Figure 1.34B. Although such surface can be made in large scale, poor mechanical stability mostly, in terms of the adhesion of these TiO_2 with substrates, hindered its applications in daily life.

1.8 Use of Organic Solvents to Fabricate Liquid Repellent Surfaces

Decreasing surface energy of materials through the functionalization with different low surface energy molecules such as alkyl silanes or fluorinated alkyl silanes have become very popular in past few decades. This is well written in the recent review by Zhang *et al* (Li *et al.*, 2016). Because of the low surface energy, these molecules are usually insoluble in polar solvents and easily get phase separated. This promotes the use of organic nonpolar solvents and mixture of various organic solvents. However, it increases concern about safety, environmental issues that is very much pronounced in the case of large-scale productions. Few methods have been developed where alcohol, mostly ethanol or methanol were used as a base solvent. Collier and coworkers (Boreyko *et al.*, 2014) have reported the modification of SiO_2 nanoparticles with perfluorooctyl-trichlorosilane (PFOTCS) in hexane. These nanoparticles were finally mixed with other PU resign in acetone and spin coated over the substrates to fabricate the superhydrophobic surface. Wong *et al* have reported the formation of the pyramidal structured superhydrophobic surface by dipping a HF/H_2O_2 etched rough silicon substrate in a PFOTCS solution in hexane (Figure 1.35) (Xiu *et al.*, 2008). Use of 1H,1H,2H,2H-perfluorodecyltrichlorosilane solution of alkane to reduce the surface energy of the glass and rough titanium surface also known in this context. (Kim *et al.*, 2011; Maitra *et al.*, 2014). Sometimes, to control the formation of silane layers over the material, inert atmosphere (N_2) is also used as silane molecules, mostly the cholorosilanes, are very sensitive towards humidity and react violently (Nguyen *et al.*, 2014). Surfaces of various metal oxide nanoparticles and others such as aluminium oxide, zinc oxide, copper oxide and copper alloys, *etc* are also modified in a similar process to impart the liquid-repelling properties (Han *et al.*, 2005; Liu *et al.*, 2012; Lee *et al.*, 2014; Chen *et al.*, 2015). Surface modification of materials having different shape and morphologies are also reported by several groups. For example, Qi *et al* have reported the fabrication of 1H,1H,2H,2H-perfluorodecyltrichlorosilane modified TiO_2 nanorod having excellent self-cleaning property. Figure 1.36 shows the microscopic images of this TiO_2 nanorod array. (Cai *et al.*, 2012).

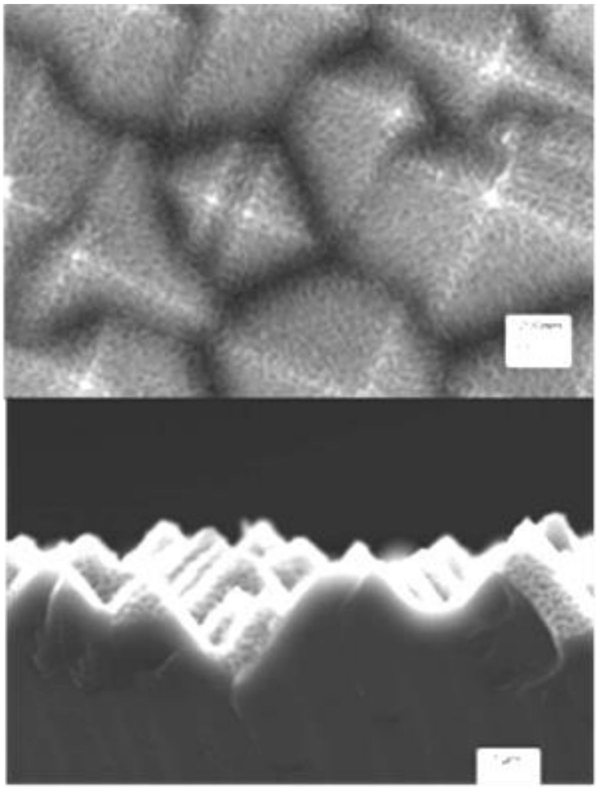


Figure1.35 SEM image of HF/H_2O_2 etched Si pyramid surface. Bottom, cross sectional image. Reproduced with permission from (Xiu *et al.*, 2008) © 2008, American Chemical Society.

Aluminium nanowire-based low surface energy surface has been developed via an anodization process followed by the treatment with 1H,1H,2H,2H-perfluorooctadecyltrichlorosilane in hexane. Liquids having low surface tension values, even lubrication fluid and water-oil emulsions were observed to sit as a sphere and roll off easily over this surface (Wu *et al.*, 2009). Recently, UV resistive superhydrophobic surface was prepared in heptane having BiOCl nanoflake structures (Li *et al.*, 2011). Suppressed photo-oxidation property of the surface in presence of UV source can be explained by the formation of an interfacial barrier between BiOCl and 1H,1H,2H,2H,-perfluorodecyltrichlorosilane (PFDTCS) layers. Similar to this, a bunch of examples exist where alkane based solvents are used predominantly to develop liquid repelling surfaces (Barthwal and Lim, 2015; Li *et al.*, 2016). In several cases, to functionalise the material with low surface energy molecules, toluene was used as a major solvent system (Zhang *et al.*, 2005; Kwak *et al.*, 2010; Ishizaki *et al.*, 2011; Campos *et al.*, 2012; Lee and Yong, 2012). For instance, zinc oxide, iron oxide and carbon nanotube-based superhydrophobic materials were synthesised in toluene (Yu *et al.*, 2013; Gu *et al.*, 2015).

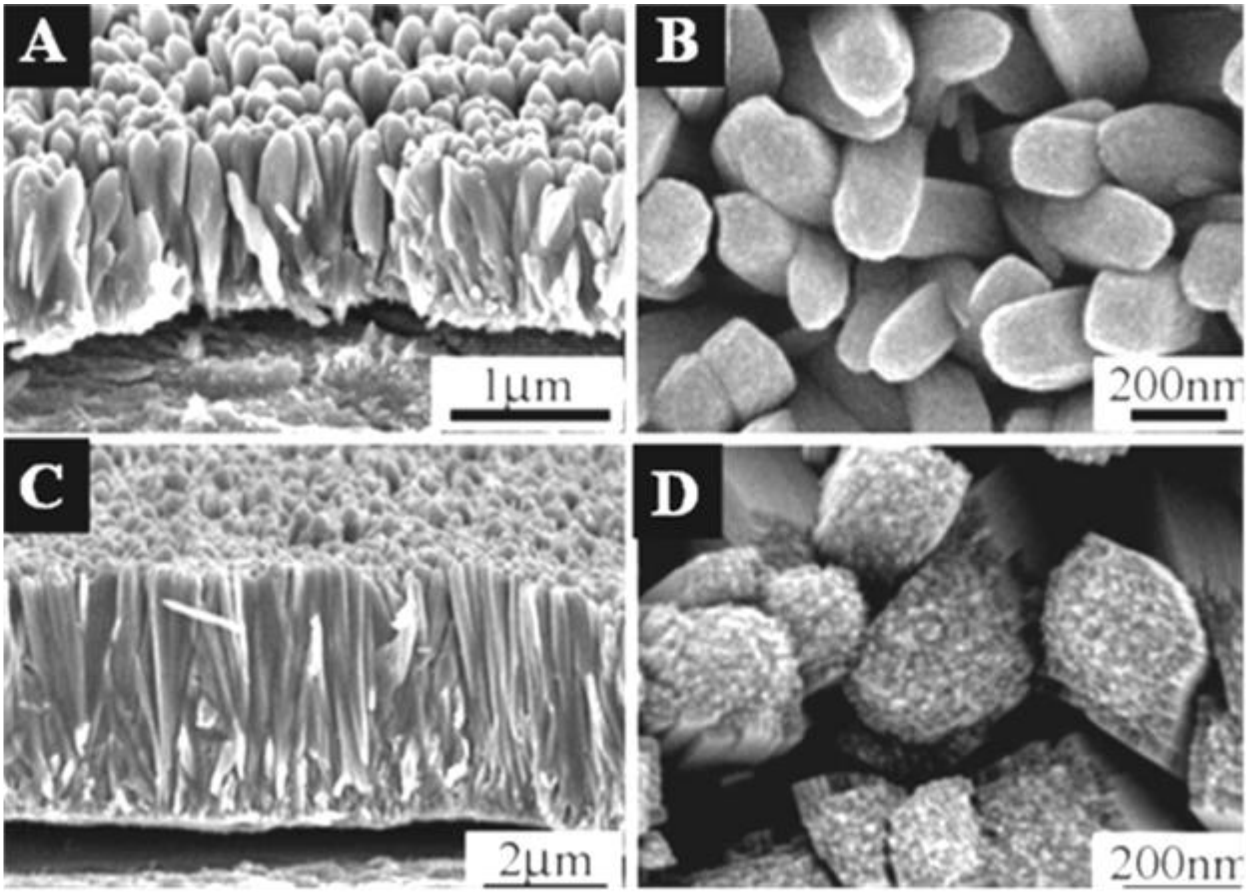


Figure1.36 SEM images of TiO_2 nanorod arrays grown at 150 °C for different times, (A,B) 2 h and (C,D) 8 h. Cross-sectional view (A,C) and top view (B,D): (a and b) 2 h and (c and d) 8 h. Reproduced with permission from (Cai *et al.*, 2012) © 2012 Royal Society of Chemistry.

Recently, Yang *et al* have demonstrated the formation of a transparent superhydro-phobic surface where various polymeric substrates were spin-coated with surface modified fluorinated oil dispersed silica nanoparticles (Figure 1.37). The coated surface showed 95% transparency which is remarkable in the view of its possible application potentials (Figure 1.37B). Here the particles were modified separately at room temperature in toluene. The extent of superhydrophobicity was measured with advancing angle and sliding angle measurements where the advancing angle was greater than 150° and sliding angle was less than 5° (Xu *et al.*, 2012). Except these, a large number of liquid repellent surfaces are known where other organic solvents and mixture of solvents were used.

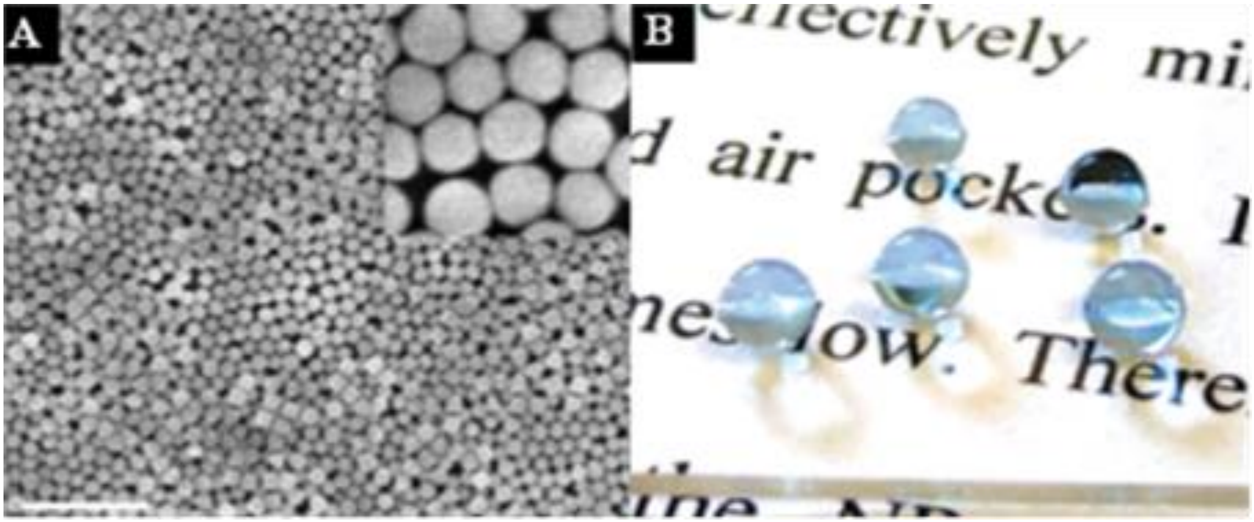


Figure1.37 (A) SEM images of spin-coated modified SiO_2 NPs (100 nm). Inset, magnified image. (B) Optical transparency of spin-coated film on glass substrate. Reproduced with permission from (Xu *et al.*, 2012) © 2012, American Chemical Society.

CHAPTER 2

Objectives and Motivation

In view of the recent progress in liquid repelling surfaces and their huge application potential, it can be clearly predicted that such multifunctional surfaces can solve many of our biggest problems of recent times and future generations including water scarcity and energy related issues. However, there is a big gap between academia and industry that limits the commercialization of such multifunctional surfaces/materials. Although various methodologies have been introduced and demonstrated to fabricate such surfaces, most of the reports refer to laboratory scale synthesis. In this perspective, several parameters can be exampled that hinder the bulk production of these surfaces/materials. This includes the involvement of complex steps, expensive starting materials and reagents, environment compatibility, limitation in the production of large area surfaces/ bulk materials, durability, affordability and many others. This enhances the necessity to develop robust nonwettable materials in an industrially feasible way. Ideally, the procedure should be similar to nature's ways of making such surfaces. For example, naturally evolved liquid repelling surfaces are made/developed at atmospheric temperature and pressure where water is predominantly used as a solvent. Also, in the context of ingredients, mostly cellulose is used which is simple, very much available and economic from industrial point of view.

These inspired us to think and develop a water-based, simple and one step methodology to prepare different coating materials at ambient conditions that will provide superhydrophobic surface once it is coated over a range of substrates irrespective of their size, shape morphology. Because of the simplicity and available various kinds of well-established coating techniques, formulating coating materials is far more adaptable, in general, both in academia and industries. It also enhances the applicability of material in various fields of science and technologies. Depending on the area and substrates, coating technique can be spin coating, dip coating, spray coating, brush coating *etc.*

To prepare a material in industrial scale, it is very important to see the commercial availability of ingredients, their costs, safety related to their usage, transportation and storage. In this perspective, cellulose and clays are the most advisable materials to start with because of their low price and huge available resources. These are already being used in different industries like paint, printing, packaging, various paper-based technology including microfluidics. On the other hand, as water is available everywhere in large quantity (irrespective of the purity), preparation based on water will lead to a decrease in production cost as well as the safety-related issues, unlike organic solvents. Moreover, it minimizes various environmental and health related issues which is the biggest matter of concern for industries. Also, from the chemistry point of view, materials like cellulose and clays are hydrophilic (or water absorbing) in nature and easily get dispersed in water which facilitates the chemical functionalization unlike organic solvents. However, this suggests that the developed methodology needs to reverse one of the physical properties of these materials, namely hydrophilicity to hydrophobicity. In this context, very few reports exist where water was used as a solvent to design superhydrophobic or superoleophobic materials. For example, Megaridis *et al* have reported the formation of the low-cost, waterborne superhydrophobic coating with ethylene copolymer and acrylic acid (Schutzius *et al.*, 2013). Wu *et al*. have demonstrated the fabrication of self-repairing coating based on UV-responsive microcapsules. This TiO_2 and SiO_2 nanoparticles-based coating was made in water and can be applied to different substrates (Chen *et al.*, 2015). Recently, Lin and coworkers have shown the preparation of durable superamphiphobic surface having self-healing property that withstand various mechanical tests. Here, a combination of polytetrafluoroethylene (PTFE) nanoparticle, perfluorodecyltriethoxysilane and a fluorinated surfactant were used to formulate the composition in water (Zhou *et al.*, 2017). However, in all of the cases, either the methodologies consist of multiple complicated steps or the reagents used in the synthesis are too expensive to implement in the industrial large-scale production systems. Therefore, there is a great need to develop an industrially feasible methodology considering all the factors discussed previously.

In view of the recent situation, my research was mostly directed towards the fabrication of bulk superhydrophobic and liquid repelling coating materials in water at ambient conditions from readily available commercial materials like clay and cellulose. One-step synthesis of these materials through an easy chemical functionalization process and their applicability over a range of substrates/surfaces that provides excellent water repelling film in room temperature demonstrate the simplicity, novelty as well as the possible industrial viability of the methodology. Application of these materials in the context of recent global issues and day-to-day applications in various fields are also addressed.

CHAPTER 3

Materials and Methods

3.1 Materials

All the chemicals were purchased from commercial sources and used without further purification. Native cellulose nanofiber (2.8 wt%) was purchased from BioPlus. These nano-fibers were also characterized with TEM and AFM (Figure 3.1). Kaolinite clay was purchased from Alpha minerals and chemicals. 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane (FS, 98%) was purchased from Aldrich. 3-(2-aminoethylamino)propyltrimethoxysilane (AS, commercial grade) was purchased from Rishichem Distributors. Ethanol, dimethyl sulfoxide, heptane, hexane, *n*-octane, benzene, toluene, dimethylformamide (DMF), tetrahydrofuran (THF), chloroform, dichloromethane, paraffin oil (AR grade) and acetone were procured from RANKEM, India. Sand paper (P320) was purchased from a local hardware shop. Peltier cooling system was purchased from a local electronics shop.

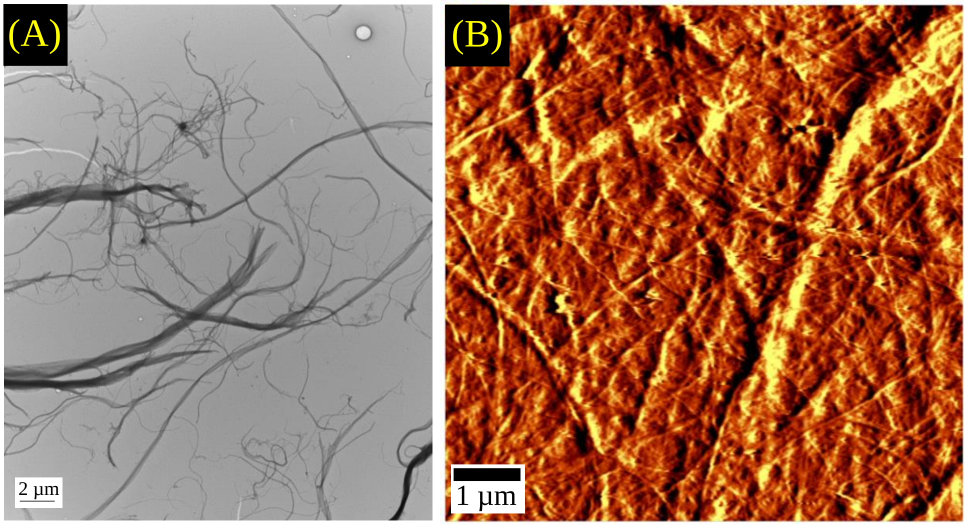


Figure 3.1 Characterization of the native cellulose nanofiber. (A) TEM image and (B) AFM image of the sample. Reprinted with permission from publication I (Baidya *et al.*, 2017) © 2017, American Chemical Society.

3.2 Methods

3.2.1 Chemical Modification of Native Hydrophilic Cellulose Nanofibers (CNFs)

Chemical modification of cellulose nanofibers (CNFs) was made through a wet chemical process in an aqueous medium where well-dispersed native hydrophilic CNF (1 wt%) was mixed with two different functional silanes, FS (0.61 v/v%) and AS (0.92 v/v%), under vigorous stirring conditions and kept for 6 to 7 h at room temperature. Before mixing with these chemicals, hydrophilic CNFs were well dispersed by sonication for 30 min in water (Figure 3.1). These chemically modified well-dispersed CNFs, obtained in a wet chemical process were diluted in water and spray coated on a glass slide (for characterization) and laboratory made hydrophilic CNF paper. Though spray coating was used to prepare all the samples, other techniques such as dip coating, doctor blading, *etc.*, are equally efficient for sample preparation. Coated samples were dried at room temperature (30 °C) and tested through various experiments. The observed morphology (macroscopic roughness) over the dried surface is related to the fibrous structure of CNF. Synthesised homogeneous aqueous dispersion (modified CNF) can be stored at room temperature in the laboratory environment for more than a year without any special precaution. Though silanization reaction is very fast in the aqueous medium, it was controlled with the solubility of FS in water which is very low because of its long hydrophobic tail. We believe that this particular fluorosilane gets adsorbed on the cellulose surface slowly due to the numerous hydroxyl groups and gets hydrolysed gradually.

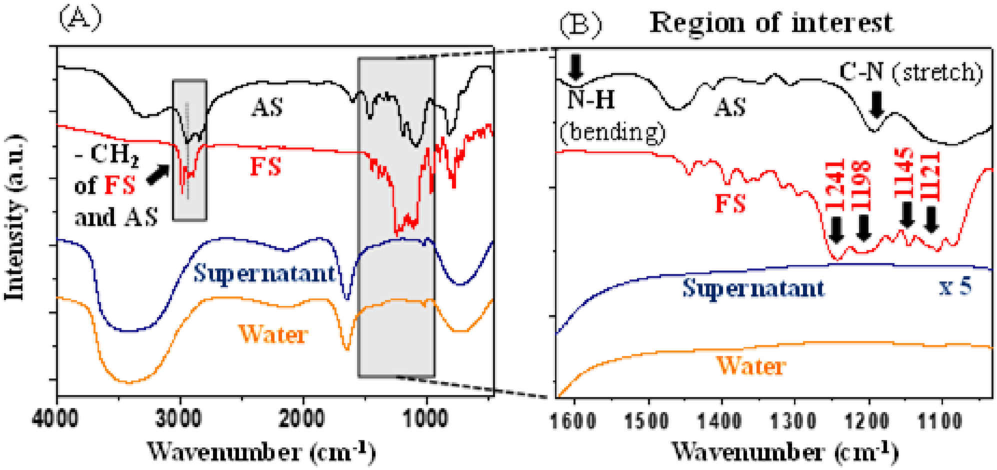


Figure 3.2 Characterization of the supernatant of modified CNF dispersion. (A) IR spectra of supernatant, AS, FS, and water. (B) Expanded view of marked area in A. IR

spectrum of supernatant (blue) does not contain any characteristic peak of AS (black) and FS (red). It is similar to pure water (orange). Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

Presence of unreacted FS and AS/Complition of the reaction between the FS and AS with CNFs was studied through IR spectroscopy where the spectrum of the supernatant solution (after centrifugation of as synthesized modified CNF dispersion) was compared with all the reagents (AS and FS) and pure water (Figure 3.2). In the Figure, spectrum of the supernatant (blue) does not contain any characteristic peak of AS (black) and FS (red). The spectrum was similar to pure water (orange). Although AS is known to be non-toxic in biological experiments (Shen *et al.*, 2014; Li *et al.*, 2015) and C-F bonds in FS are stable, they may be used with caution.

3.2.2 Preparation of Superhydrophobic/Waterproof Paper

The waterproof paper was prepared by spraying waterborne chemically functionalized CNF dispersion on laboratory-made hydrophilic native CNF paper. Such CNF paper was prepared through the evaporation method where homogeneous CNF solution was poured carefully in a plastic petridish maintaining the homogeneity of the solution everywhere in the solution bed. Once the solution was dried properly at room temperature, the film was taken out by applying mild heat (30-35 ºC) and was used to prepare superhydrophobic/ water repellent paper with modified CNF coating. In short, as synthesised aqueous dispersion of modified CNF composite was diluted with water at 1:2 volume ratio and sprayed on laboratory made hydrophilic CNF papers. Later it was dried at room temperature (30 ºC) and tested with different experiments.

3.2.3 Long Term Stability of Modified CNF Made Waterproof Paper

Long term stability of the coating was checked in two ways. Firstly, the synthesized material was kept at laboratory environment for 6 months and later on coated on the surface. No difference in water repelling property of the coated surface was observed compared to the surface coated with the freshly prepared material. Secondly, immediately after synthesis, the surface was coated with the material and kept at laboratory environment for 6 months. In this case also, similar water repelling property was observed compared to the surface coated with the freshly prepared material. To check the stability of the chemical attachment between FS and AS with CNF, the superhydrophobic surface (modified CNF coated) was sonicated in a water bath for 30 mins and the water was examined using IR spectroscopy along with all the used reagents (AS and FS) and pure water (Figure 3.3). The spectrum of ‘water after sonication’ (purple) does not contain any characteristic peak of AS (black) and FS (red). However, it is similar to pure water (orange). Please note that characteristic peak of AS and FS are marked in the spectrum which are absent in water after sonication with the coated surface. The study confirms that under normal conditions, the coating does not degrade.

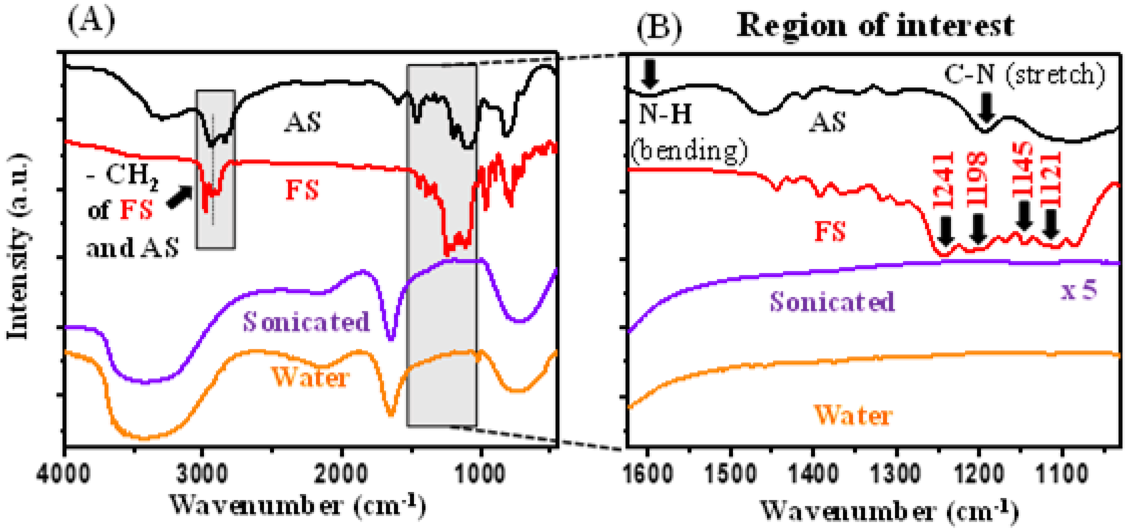


Figure 3.3 Long term stability test of chemically attached FS and AS with CNF. (A) IR spectra of ‘water after sonication’, AS, FS, and water. (B) Expanded view of marked area in A. IR spectrum of ‘water after sonication’ (purple) does not contain any characteristic peak of AS (black) and FS (red). It is similar to pure water (orange). Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

3.2.4 Abrasion Resistance of Modified CNF Made Waterproof Paper

Multiple abrasion tests such as sand paper abrasion with a load of 50 g, scratching with a knife, finger wiping and tape adhesion tests were performed to evaluate the abrasion resistance and adhesion strength of the coating on different substrates (glass and laboratory made paper). For sand paper abrasion, a piece of sand paper (P320) was kept between the coated glass surface with a load of 50 g, and the set up was moved for 5 cm along the coating. After completion of 10 cycles, the wettability of the abraded surface was tested with both jet motion and CA of water droplets. This experiment was further repeated with multiple cycles. A similar methodology was adopted for the finger wiping test, where the surface was rubbed back and forth multiple times with thump and subjected to water flow and CA measurements. For knife scratching and tape adhesion tests, surfaces were evaluated with similar water jet motion and CA measurements after each experiment and the same was repeated 10 times.

3.2.5 Durability of Modified CNF Coated Surface upon Cyclic Thermo-Chemical Perturbations

Durability of the coating was evaluated by measuring the static CA of water droplet on the tested surface. Various external stresses such as (Set-1) exposure to various organic fluids, (Set-2) high temperature treatment, (Set-3) low temperature treatment and (Set-4) exposure to direct sunlight (longevity test) were used to test the surfaces. Stability of the water repelling coating upon chemical stresses was tested by keeping the coated surface within various organic fluids for 1 h. Different polar and nonpolar solvents like ethanol, tetrahydrofuran (THF), dimethylformamide (DMF), toluene and hexane were used to simulate chemical damages. After each solvent treatment, the surface was dried at room temperature and CA of water droplet was measured. Each solvent was tested 2 times. Thermal effects on the surface in extreme conditions were performed by keeping the surfaces at 200 °C and -80 ˚C for 2 h (Set -3). Effect of direct sunlight on the coated surfaces was tested upon exposing it outside for 2 months (Set- 4). While the same coated glass surface was used 10 times in cyclic fashion for each set (for Set-1, Set- 2 and Set- 3), due to time constraints, 10 different surfaces were used to perform the Set 4 experiment.

3.2.6 Antibacterial and Antifungal Properties of Modified CNF Made Waterproof Paper

Interaction of bacteria with the superhydrophobic paper was tested on equally sized paper samples using gram-negative *Escherichia coli* (ATCC 10536). *E. coli* was inoculated in 10 mL of Luria Bertani Broth (LB) (Himedia) and incubated overnight in an air bath shaker at 37 °C and 300 rpm to reach the exponential growth phase. The bacterial solution was centrifuged at 3000 rpm for 5 min to remove the used media and washed twice with sterile saline. The suspension was diluted 1,000× in sterile saline. Using the spread plate method, plating concentrations were determined as 10^5 colony forming units (CFU)/ mL. For testing the bacterial resistance property, the coated and uncoated papers were surface sterilised and dipped in the bacterial solution for 2 min. Substrates were tilted at 90° to allow the bacterial solution to roll off, if possible. Subsequently, samples were rinsed with 50 μL of sterile saline. The surfaces of the substrates were then stamped face-down in MacConkey agar plates (Himedia) to transfer residual bacteria. The agar plates were incubated for 24 h at 37 °C in an incubator. Images were taken after 24 h and bacterial growth in coated and uncoated paper samples was compared. Agar was prepared prior to experiments according to the manufacture's protocol. For interaction of fungi with the superhydrophobic paper, isolated airborne *Aspergillus sp.* was placed beside the equally sized test paper samples. This paper was placed on a square block of potato dextrose agar in a petri dish. A sterile moist cotton was also placed inside the petri dish to maintain the humidity. This set-up was incubated for 4 days at 25 °C until visible spores appeared.

3.2.7 Chemical Modification of Native Hydrophilic Clay Particles

The waterborne superhydrophobic material was synthesised by an easy chemical modification of kaolinite clay at room temperature with two functional silanes. Chemically, these aluminosilicate clay sheets consist of numerous hydroxyl groups on the surface which are reactive in the well-dispersed condition in water. In the synthetic protocol, water dispersed clay sheets (6 wt%) were mixed with two different functional silanes, 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FS, 2 wt%) and 3-(2-aminoethylamino)propyltrimethoxysilane (AS, 1 wt%) and kept under vigorous stirring conditions for 6 to 7 h. Whereas silanization reaction in general is very fast in aqueous medium, because of the low solubility of FS in water, at first it gets adsorbed on the clay surface and hydrolyzes slowly in water and gets attached covalently to the clay surface (Teisala *et al.*, 2014). Thus, a water dispersed functionalized clay composite was obtained and spray coated on different substrates followed by drying at room temperature. Quantitatively, 1 mL of the as-prepared composite solution was mixed with water in 1:1 ratio and sprayed over a glass slide and a paper, having an area of 75x26 mm^2. Upon drying at room temperature (30 °C), a superhydrophobic film of nearly 8 micron thickness (on a glass surface) was obtained which shows a high CA> 170° (±2°) and low CAH< 5° (±2°) for water. However, to facilitate faster evaporation, the coated substrates were dried in warmer condition (45 °C) occasionally, without affecting the properties of the material. Later on, this water-based material was stored at room temperature in the laboratory environment for more than a year without any special precaution.

3.2.8 Durability of Modified Clay Coated Surface upon Cyclic Mechanical Perturbations

The durability of the coating was tested by measuring the static contact angle (CA) of water droplets after imparting cyclic mechanical stresses on the surfaces. Hard mechanical stresses include scratching with knife and sand paper abrasion test. For scratching with a knife, 10 different scratches were made on the same surface and subjected to CA measurements after every scratch. Sand paper abrasion test was performed by keeping a sand paper between the coated surface with a load of 50 g and the sand paper was moved 10 complete cycles over the surface. CA of water droplets was measured after every 10 cycles and continued similarly for 10 times. Soft mechanical stresses were induced in the form of tissue paper abrasion and finger wiping abrasion. Same methodology (mentioned above) was used in this case also. For each test (both hard and soft mechanical stresses) the same surface was used repeatedly.

3.2.9 Durability of Modified Clay Coated Waterproof Paper

Durability of the flexible waterproof paper was tested with induced mechanical abrasions and various environmental stresses. For mechanical abrasion, sand paper abrasion (with a load of 50 g) and finger wiping tests, samples were evaluated through static CA and CAH measurements after every 10 complete cycles where each cycle consists of back and forth movements for 5 cm each. Environmental stresses like direct sunlight exposure and effect of bending/ twisting of waterproof paper were also studied with CA and CAH measurements. For effect of direct sunlight exposure, the coated paper was kept under sunlight and evaluated with CA and CAH measurement after each 5 h of exposure. This was further continued 10 times. For bending/ twisting tests, the coated paper was twisted in different possible ways (90º, 180º, rolling, *etc.*) and CA and CAH were checked after every 10 cycles of twisting. The data are plotted in Figure 5C.

3.2.10 Bacterial Resistance of Modified Clay Coated Surface

Bacterial resistance test was done with Gram-negative *Escherichia coli* (ATCC 10536). Details of the experiments is stated before in section 2.2.6. In short, *E. coli* was inoculated in 10 mL of Luria−Bertani broth (LB) (Himedia) and kept overnight in an air bath shaker at 37 °C and 300 rpm to reach the exponential growth phase. Later, the bacterial solution was centrifuged at 3000 rpm for 5 min to remove the used media and washed twice with sterile saline. The suspension was diluted further to make the plating concentrations as 107 colony forming units (CFU)/ mL. This was measured by using the spread plate method. Resulting solution was used for the bacterial resistance experiment.

3.2.11 Synthesis of Liquid Repellent Slippery Coating Material

In the synthesis protocol, two different functional silanes, perfluorooctyltriethoxysilane (FS) (1.8 v%) and aminopropylaminoethyltrimethoxysilane (AS) (40 v%), were added in water and stirred for 6 to 7 hours at room temperature. The final composite was in liquid form and was coated on various substrates by spray coating and was cured in an oven at 110 ˚C for 2 hours. Although spray coating technique was used to prepare the samples, other methods like spin coating, dip coating and doctor blading methods may be used to prepare the samples without compromising the transparency of the surface. While the thickness of the coating can be modified depending on the volume of the material used, nearly 100 microliter of the as synthesized composite material was sprayed to make a thin film on a surfaces area of 75 x 26 mm^2. To demonstrate the wide applicability of this material, different types of substrates were coated and tested for material compatibility and mechano-thermo-chemical stability. These are explained and demonstrated later in the text. Although AS is known to be non-toxic in biological experiments and C-F bonds of FS are stable, the formulation can be used with caution.

3.2.12 Stability of Liquid Repelled Slippery Surface upon Cyclic Thermo-Mechano-Chemical Perturbation

To measure the durability of the material, the coated surface was tested with cyclic thermo-mechano-chemical perturbations. For all experiments (Set-1,2,3 &4), the same surface was used repeatedly. Change in wettability after each cycle of every set was tested with static CA and CAH measurements. Here, water and toluene were used as test liquids. To test thermal stability, the coated surface was treated at high (200 ˚C, set-1) and low temperatures (-80 ˚C, set-2), respectively for 5 h in every cycle. This was repeated for 5 times for both the cases. For assessing chemical inertness, the coated surface was dipped inside the solvent and kept for 2 h. Various polar and nonpolar solvents like ethanol, THF, DMF, hexane, silicone oil and an emulsion (a mixture of paraffin oil and water) were used to simulate chemical strain. To quantify the effect of direct sunlight, coated surfaces were exposed to sunlight and checked at regular time intervals of 8 h for a duration of 40 h.

3.2.13 Tilting Angle Experiment over Transparent Slippery Surface

To measure the extent of slipperiness, movement of a water droplet upon tilting the slip surface was captured by camera and its velocity was calculated, which is directly related to the friction or slipperiness of the coated surface. The motion was induced by tilting the surface manually.

CHAPTER 4

Waterborne Superhydrophobic Material from Cellulose Nanofiber Building Blocks

4.1 Overview of Work

In view of a great demand for paper-based technologies, nonwettable fibrous substrates with excellent durability have drawn much attention in recent years. In this context, the use of cellulose nanofibers (CNFs), the smallest unit of cellulosic substrates (5−20 nm wide and 500 nm to several microns in length), to design waterproof paper can be an economical and smart approach. In this study, an eco-friendly and facile methodology to develop a multifunctional waterproof paper via the fabrication of fluoroalkyl functionalized CNFs in the aqueous medium is presented (Figure 4.1). This strategy avoids the need for organic solvents, thereby minimizing cost as well as reducing safety and environmental concerns. Besides, it widens the applicability of such materials as nanocellulose-based aqueous coatings on hard and soft substrates including paper, in large areas. Water droplets showed a contact angle of 160° (±2°) over these surfaces and rolled off easily.

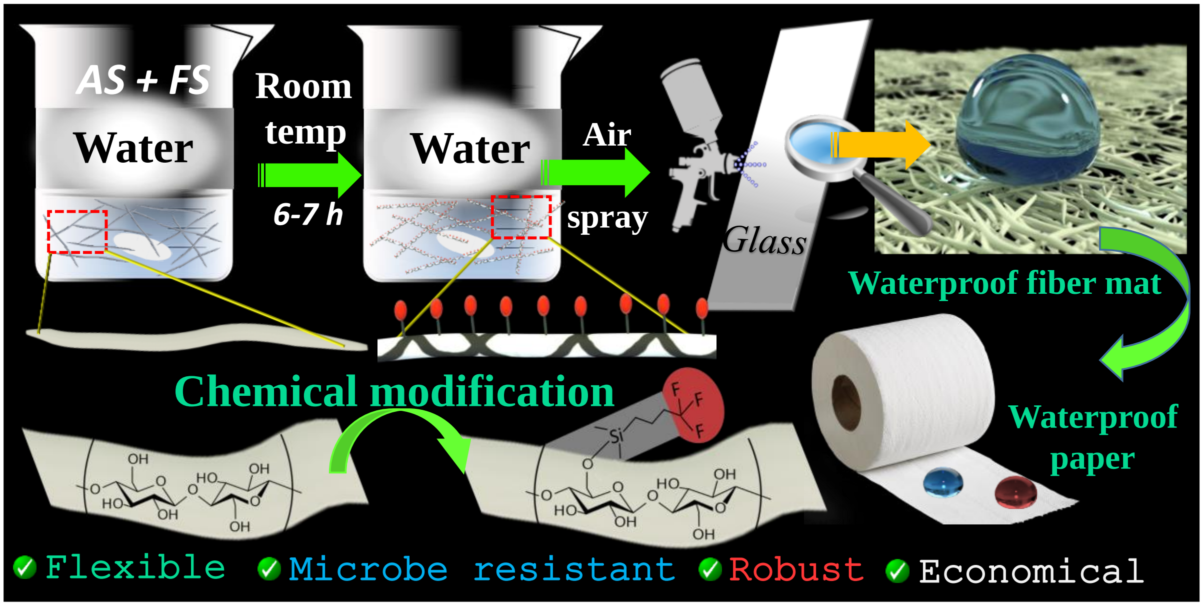


Figure 4.1 Schematic representation of the overall work. Adapted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

While native CNFs are extremely hydrophilic and can be dispersed in water easily, these waterborne fluorinated CNFs allow the fabrication of a superhydrophobic film that does not redisperse upon submersion in water. Incorporated chemical functionalities provide excellent durability toward mechanochemical damages of relevance to daily use such as knife scratch, sand abrasion, spillage of organic solvents, *etc.* Mechanical flexibility of the chemically modified CNF composed paper remains intact despite its enhanced mechanical strength, without additives. Superhydrophobicity induced excellent microbial resistance of the waterproof paper which expands its utility in various paper-based technologies. This includes waterproof electronics, currency, books, *etc.*, where the integrity of the fibers, as demonstrated here, is a much-needed criterion.

4.2 Introduction

As a convenient way to tune the characteristic properties of various materials, surface engineering has become one of the most important research areas of recent decades. Various techniques such as plasma deposition (Pakdel *et al.*, 2014), chemical vapor deposition (CVD) (Choy, 2003), atomic layer deposition (ALD) (Kemell *et al.*, 2005), nanoparticle deposition (Rao *et al.*, 1998), and sol-gel methods (Lu *et al.*, 1997) have been developed to create micro/nanoscale coatings that essentially control the properties of materials by introducing functionalities on the surface. Among these, developing materials with tunable surface wettability is one such interesting research direction that expanded to several potential applications such as self-cleaning (Sun *et al.*, 2005; Park *et al.*, 2012; Zhang *et al.*, 2013), anticorrosion (Liu *et al.*, 2008), water-oil separation (Kwon *et al.*, 2015; Li *et al.*, 2016), anti-icing (Mishchenko *et al.*, 2010; Golovin *et al.*, 2016), drag reduction (Jung and Bhushan, 2009; Golovin *et al.*, 2016), sensing (Xu *et al.*, 2015; Zhang *et al.*, 2016), atmospheric water capture (Parker and Lawrence, 2001; Zheng *et al.*, 2010), construction materials (Husni *et al.*, 2017), microfluidic devices (Li *et al.*, 2016), smart windows (Lee *et al.*, 2010), *etc.* Surfaces with low surface energy also minimize bacterial adhesion which essentially prevents the growth of biofilms, known as biofouling (Leslie *et al.*, 2014; Dou *et al.*, 2015; Hizal *et al.*, 2017; Hou *et al.*, 2017). Mother nature is bestowed with such surfaces which are characteristic of several species of plants, insects, animals, and birds, *etc* (Gao and Jiang, 2004; Feng *et al.*, 2008; Bixler and Bhushan, 2014). In this account, lotus leaves, water striders, and rose petals have already been studied in great detail. Surface roughness (nano/microscale) and controlled chemical functionalities are the underlying reason for such phenomena (Lv *et al.*, 2016). While different approaches have been introduced (Wu *et al.*, 2011; Lee *et al.*, 2012; Zhou *et al.*, 2013), in most of the cases, surface compatibility, complicated manufacturing processes, cost, and limitation of large-scale production restrict the use of such surfaces in real life applications (Wang *et al.*, 2015). Meanwhile, availability of different chemically functionalizable materials has enhanced the interest to design such materials by wet-chemical techniques (Chen *et al.*, 2015; Lu *et al.*, 2015) that are applicable on various substrates of non-identical surface morphology through easily accessible coating processes. Clays (Mates *et al.*, 2014), polymers (Tiwari *et al.*, 2010), oxide nanoparticles (Li *et al.*, 2016), cellulosic materials (Teisala *et al.*, 2014; Chen *et al.*, 2015), *etc.* are often used as templates for the same. Yet, stability, strength, and adhesion of such coatings are the limiting factors (Wen *et al.*, 2015). For instance, small mechanical perturbations like gentle touch with tissue paper or finger wiping can damage these surfaces permanently (Verho *et al.*, 2011; Tian *et al.*, 2016). The nano and/or microscale structures that support the trapped air layer get damaged easily by mechanical abrasion, leading to failure of the Cassie state of wetting. Therefore, there is a need to design a material that provides superhydrophobic films of sufficiently robust nature for real-life applications.

Cellulose-based materials are economical, green, sustainable, and biodegradable and are increasingly investigated both in research and industry (Morales-Narváez *et al.*, 2015; Zhong *et al.*, 2015). Even though the presence of a large number of functionalizable hydroxyl groups makes it hydrophilic, different forms of cellulose fibers such as napkins, papers, cotton, *etc.* are developed to exhibit nonwettable properties (Sousa and Mano, 2013; Teisala *et al.*, 2014). Recently, Zhang and co-workers and Li and co-workers have developed hydrophobic/lipophobic paper-based sensors where fibrous substrates were treated with different fluoroalkyl silane compounds to demonstrate non-wettability. However, such surfaces have not been built starting from cellulose nanofibers (CNFs), the smallest subunit of cellulosic materials. In addition, for such materials to be industrially viable, synthesis in the aqueous medium is needed. Though a few reports on waterborne superhydrophobic materials are known (Schutzius *et al.*, 2013; Ye *et al.*, 2017), in most of the cases, organic solvents are used extensively as the primary solvent medium (chapter 1, Section 1.8) which limit the dispersibility of hydrophilic CNFs. In addition, use of organic solvents also raises a concern regarding the safety, environmental pollution, and cost of production. Therefore, fabrication of waterborne superhydrophobic materials starting from CNFs is desirable.

Here, an easy strategy to develop a multifunctional flexible waterproof paper through the chemical modification of hydrophilic native CNFs in water is reported. As a well-dispersed liquid material, it was also used for creating superhydrophobic coatings over various substrates. While coated surfaces show excellent durability upon various chemical and mechanical damages, incorporated functionality induces enhanced strength and integrity of the waterproof paper upon exposure to water for extensive periods. This material also exhibits inhibition to both bacterial and fungal growth in the cellulosic material. Being synthesized in water at room temperature and at neutral pH, environmental concerns are eliminated. We also demonstrated the extent of water resistivity and enhanced integrity of the waterproof paper for use in paper-based flexible electronics, the publishing industry, and currency printing. The science presented here is useful in converting waste to wealth in the form of superhydrophobic paints, packaging materials, affordable sensors, *etc.*

4.3 Results and Discussion

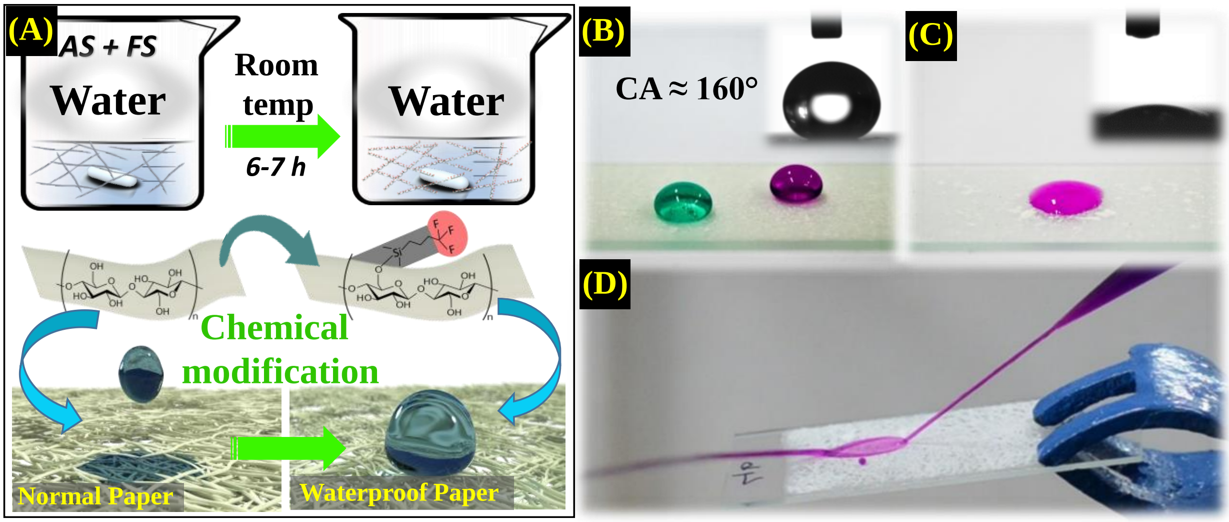


Figure 4.2 (A) Schematic representation of cellulose nanofibers (CNFs)-based waterborne superhydrophobic material, the building block of waterproof paper. (B&C) Water droplet on modified and native CNFs coated surface. Inset, the static contact angle of the water droplet. (D) Continuous jet flow on coated glass. $KMnO_4$ and $NiSO_4$

aqueous solutions were used in B, C and D, respectively, instead of pure water to have color contrast. Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

Figure 4.2A illustrates the synthesis of chemically modified/ fluorinated CNFs in water that forms excellent water repelling thin films upon coating over various substrates. Briefly, native hydrophilic CNFs were chemically functionalized with two different functional silanes, 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FS) and 3-(2-aminoethylamino)propyltrimethoxysilane (AS) by a wet chemical process in water at room temperature and spray coated both on hard (glass) and soft (paper) substrates. Though nanoscale cellulose fibers impart surface roughness, an important parameter to achieve nonwetting property, the hydroxyl groups present on such surfaces make them hydrophilic. However, these active functional groups also facilitate the covalent attachment between CNFs and silane molecules, FS and AS. Thus, a complete reversal of the hydrophilic property of cellulose not only increases the wetting resistance of the coating but also forces water to sit as a droplet (Figure 4.2B). This minimizes the air-water-solid interaction energy on the superhydrophobic surface, unlike unmodified CNFs-coated surface where water spreads easily (Figure 4.2C). The extent of the water repelling property of the coated surface was also demonstrated by rolling off or jet motion of water drops on the modified CNFs-coated substrate (Figure 4.2D).

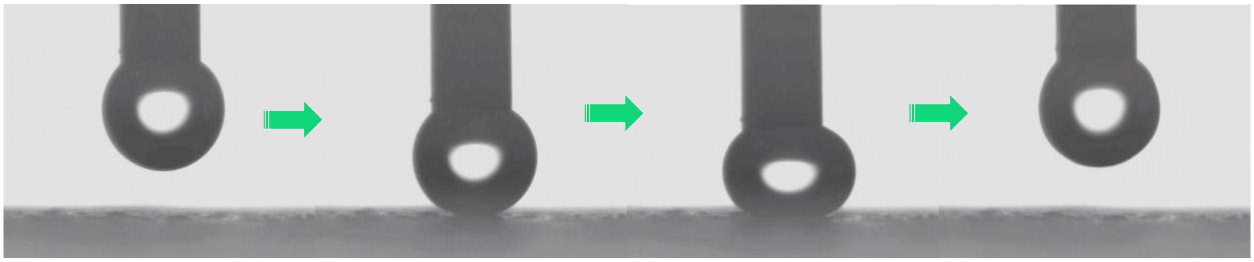


Figure 4.3 Droplet pinning test: Dragged water droplet (~ 2 μL). Droplet moved back and forth 5 cm on coated surface without any sign of pinning. Reprinted with permission from publicationI, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

This was further studied with a droplet drag experiment where water droplet (~2 μL) attached with a needle was dragged back and forth over the coated surface by 5 cm. Deformed shape of the water droplet during the experiment can be related to contact angle hysteresis (CAH) which is the result of fibrous structure induced macroscale roughness of the prepared film (Figure 4.3). This was also observed during the roll off angle measurement. Water droplet having a volume ≥10 μL rolls off easily with a roll-off angle <10° (±2°). However, for smaller volume droplets, they did not either roll off or stick to the surface and immediately flew off with a gentle blow of air.

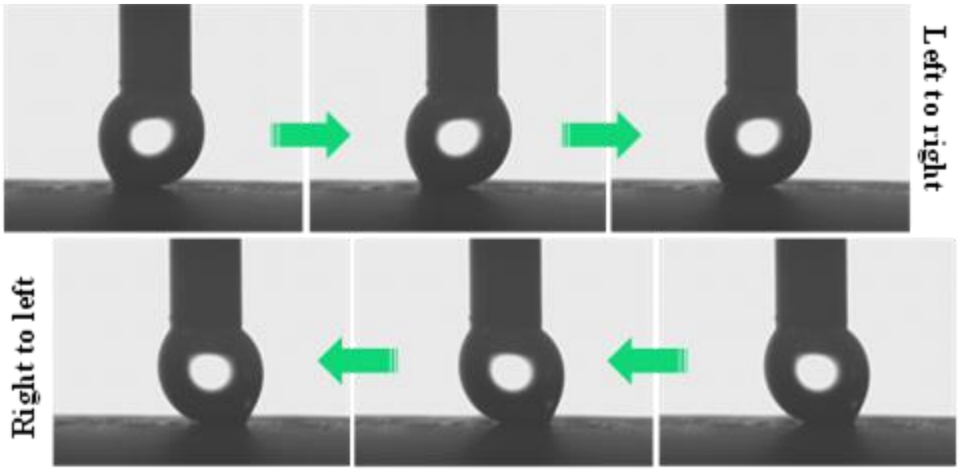


Figure 4.4 Vertical drop test. Volume of water drop ~ 2 μL. Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

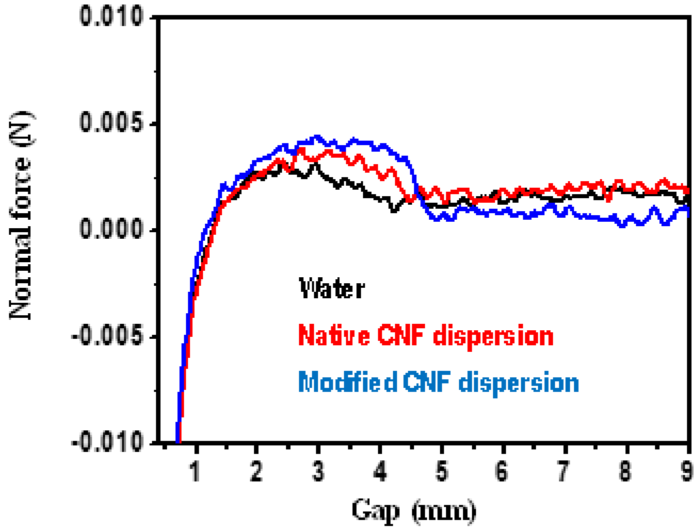


Figure 4.5 Tackiness measurement. Both native and modified CNF show water-like nature. Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

Excellent water repellent property of the material was also evaluated with a vertical drop adhesion test for multiple cycles where a water droplet (~2 μL) was seen to detach from the superhydrophobic surface without leaving any trace (Figure 4.4).

Modified CNF-coated superhydrophobic surfaces (glass) showed excellent durability when they were subjected to mechanical damages (presented below). These experiments also reflect the extent of adhesion of the material on different surfaces without any adhesive (e.g., glass and paper). This binding ability of the material originates from the chemical functionalities incorporated in the CNFs. Tackiness of the modified CNF dispersed solution was compared with native CNF dispersion and pure water (Figure 4.5). CNF concentrations in both the cases (modified and native) were the same. Interestingly, water-like nature was observed for both the dispersions. In contrast, the same modified CNF forms a rugged coating that did not show any tackiness.

Ruggedness of coating was studied through various methods of mechanical abrasion tests. Initially, the coated surfaces were subjected to knife scratch and peel-off tests (Figure 4.6A,B). Despite having a few scratches on the surface, the exposed underlying layers of the coating recover/retain a superhydrophobic nature of the surface and made water drops roll off through the damaged areas. Interestingly, a similar response was observed after a peel-off test of the surface. Durability of the coating was further tested against sand paper abrasion with a load of 50 g and a finger wiping experiment (Figure 4.6C,D), wherein the surfaces were abraded for a length of 5 cm, back and forth. For all the tests, contact angle (CA) of water droplets was measured after each of the 10 consecutive cycles and plotted in Figure 4.6E (for knife scratch test, in every cycle, one scratch was made on the coated surface).

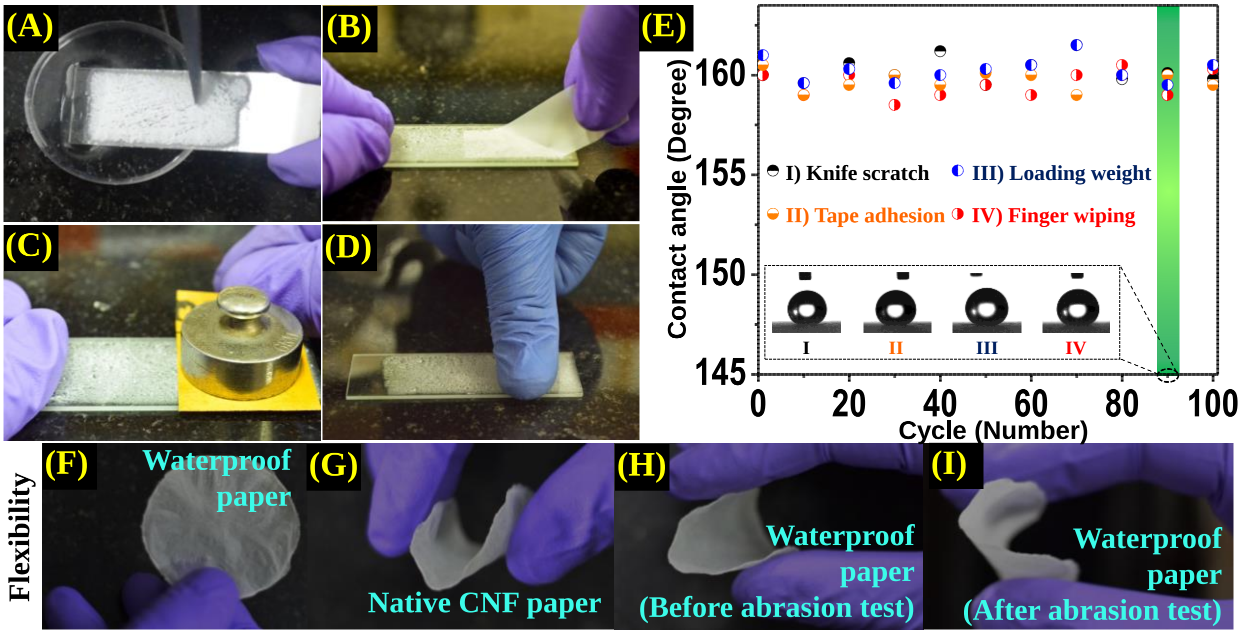


Figure 4.6 Mechanical damages induced on modified CNFs coated glass surface. (A) Scratching with a knife, (B) tape adhesion test, (C) sand paper abrasion with 50 g of load and (D) finger wiping. (E) Durability test for the water repelling surface.

Change in CA of water droplet during multiple abrasion cycles. One experiment consists of 10 complete abrasion cycles. (Inset) Photograph showing static contact angle of water on mechanically tested surfaces (after the 9th experiment, i.e., 90th cycle). (F-I). Physical appearance and flexibility of waterproof paper before and after abrasion tests. Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

Negligible variation in static CA over the mechanically perturbed surfaces implies the robustness and stability of the coating. Similar mechanical robustness with retention of superhydrophobicity was also observed for the waterproof paper upon the above-mentioned abrasion tests (except knife scratch test). Notably, mechanical flexibility of the abraded paper remained unchanged compared to native CNF paper and unabraded waterproof paper (Figure 4.6F−I). This was tested manually by bending the paper multiple times. However, the mechanical strength for the waterproof paper was enhanced (Figure 4.7) compared to native CNF paper (uncoated). We believe that the incorporated chemical functionality (secondary amine) on the CNFs which gets self-polymerized at room temperature, increases the adhesion between the fibers as well as with the substrate leading to durability of the coating. Long-term stability of the coating (while it was coated on a surface and in the dispersion form) as well as the attachment of FS and AS with CNFs were also studied in detail and explained in the chapter 3.

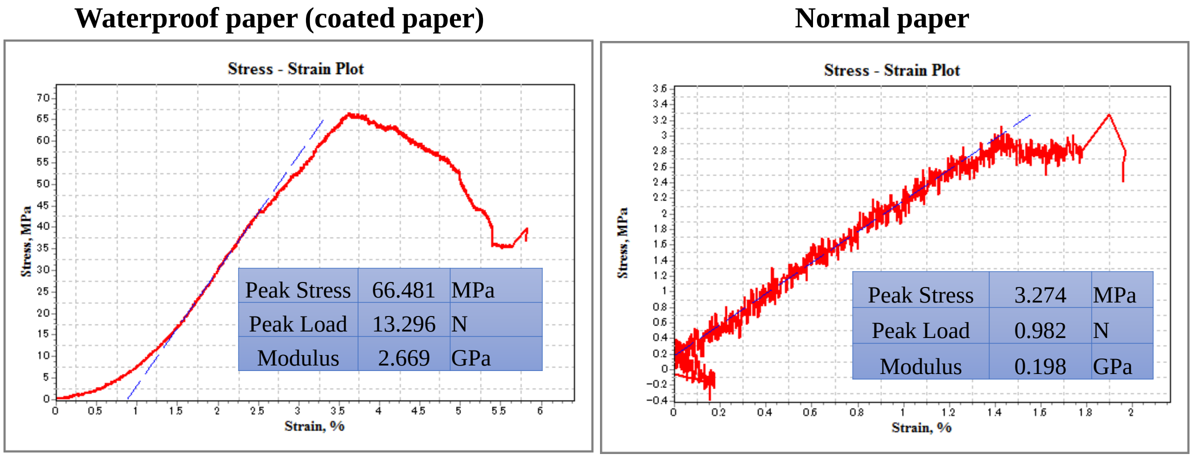

Waterproof paper (coated paper) **Normal paper**

Figure 4.7 Mechanical strength of modified cellulose nanofiber composed waterproof paper (without any adhesive). This is compared with the unmodified cellulose nanofiber paper. Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

Surface characteristics of chemically functionalized CNF coated glass substrates were studied with AFM and SEM. Increased surface roughness of the order of 200 nm was observed for the modified CNF-coated film (Figure 4.8A,B) compared to native CNF-coated film. This may be a result of the hydrophobic effect (Meyer *et al.*, 2006), namely an interaction between water and low surface energy molecules (here, fluorinated CNFs), leading to the more organized surface structure of fluorinated CNFs by minimizing the interaction energy during drying. Similar rough surface morphology was also observed in SEM (Figure 4.8C,D).

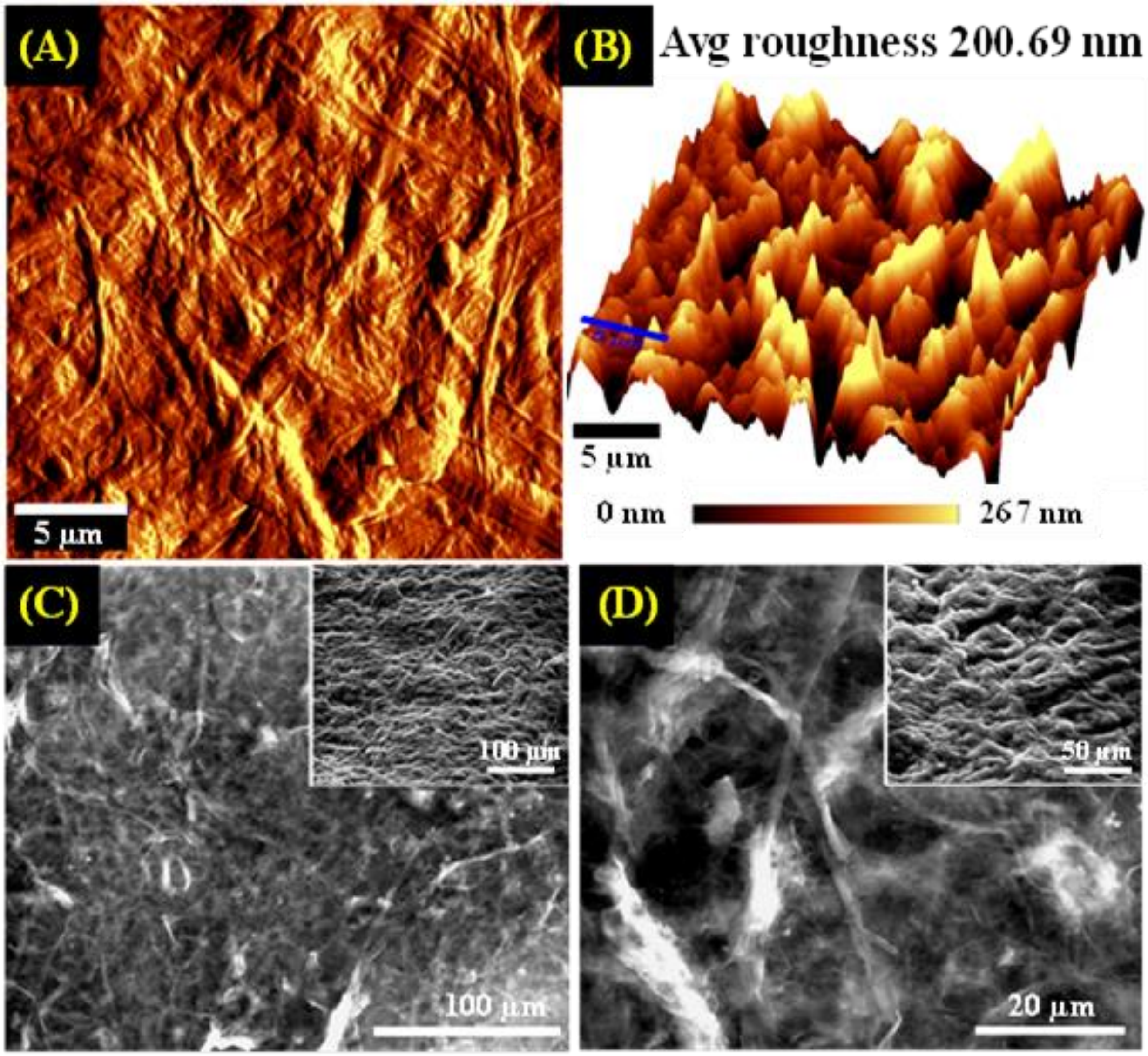
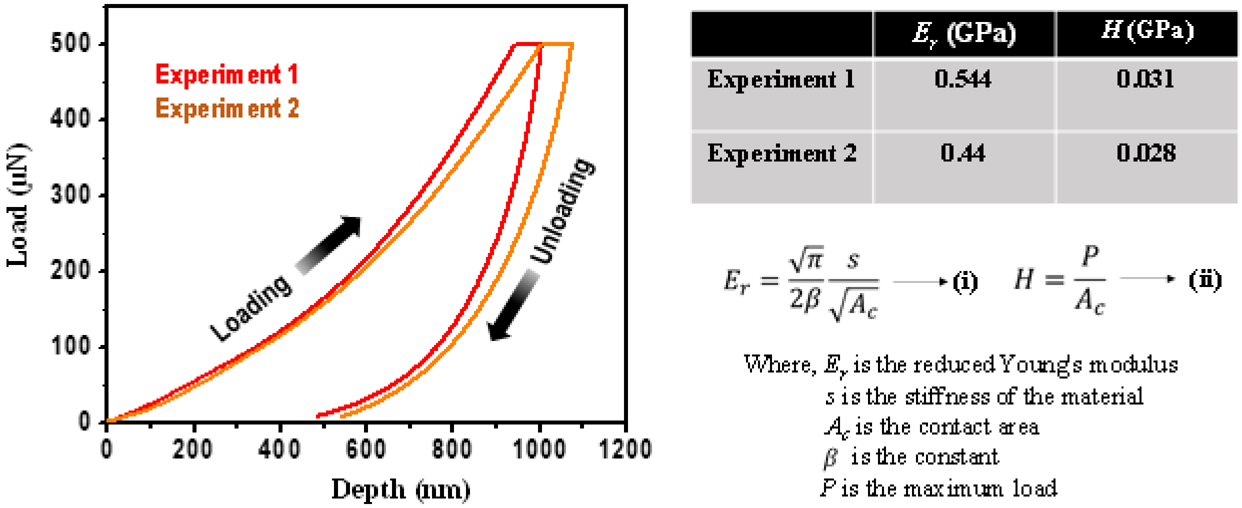


Figure 4.8 Characterization of the modified CNF coated thin film. AFM image of the coated glass substrate, 2D view (A) and 3D view (B). (C,D) SEM images in different magnifications showing the inherent roughened fibrous nature of the film. Inset,

tilted (45°) view showing the roughness of the surface. Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

The reduced Young's modulus (E_r) and hardness (H) of the modified CNF were measured through nanoindentation tests (Figure 4.9). The loading part of the load−displacement curve is elastic-plastic in nature. The slope of the initial part of the unloading curve was used to measure the stiffness(s). The values determined at 500 µN peak load are shown in the table of Figure 4.9. The E_r and H values corresponding to 500 µN can be considered as representative bulk values obtained using equations (i) and (ii) (below table in Figure 4.9), respectively.



	E_r (GPa)	H (GPa)
Experiment 1	0.544	0.031
Experiment 2	0.44	0.028

$$E_r = \frac{\sqrt{\pi}}{2\beta}\frac{s}{\sqrt{A_c}} \longrightarrow \text{(i)} \qquad H = \frac{P}{A_c} \longrightarrow \text{(ii)}$$

Where, E_r is the reduced Young's modulus
s is the stiffness of the material
A_c is the contact area
β is the constant
P is the maximum load

Figure 4.9 The reduced Young's modulus and hardness of the modified CNF (coated on glass). The values determined at 500 µN peak load are shown in the Table. The E_r and H values corresponding to 500 µN can be considered as representative bulk values obtained using equations (i) and (ii), respectively. Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

Chemical composition as well as the nature of the chemical bonding of the foreign molecules, which are considered to be the underlying reasons for both stability and robustness of the material, were characterized in detail with XPS and IR spectroscopy (Figure 4.10). The presence of two chemically different carbons, that is, (i) cellulosic carbons (C−C/C−O/ O−C−O) and (ii) carbon attached with fluorine (C−F bond in FS) in the deconvoluted C 1s spectrum of the modified CNF sample, confirmed the covalent linkage of molecules with CNFs (Figure 4.10A). These features of carbon were not seen in native CNF (Figure 4.10B). The C−C, sp^3 bonded carbon gave a peak at 284.6 eV which remained unchanged for both modified and native CNFs. However, the peak for C−O and O−C−O shifted slightly to a lower binding energy value (0.6 eV), suggesting the formation of a bond between Si (from AS or FS) and OH (from CNF). Carbons attached with fluorine appear in the higher binding energy region of the XPS spectrum (291−293 eV), as fluorine polarizes the C−F bond (Figure 4.10A). Peaks at 686.9 and 684.5 eV of the XPS survey spectrum correspond to the deconvoluted F 1s peak of C−F bonds ($-CF_2$ and $-CF_3$, respectively) (Figure 4.10C).

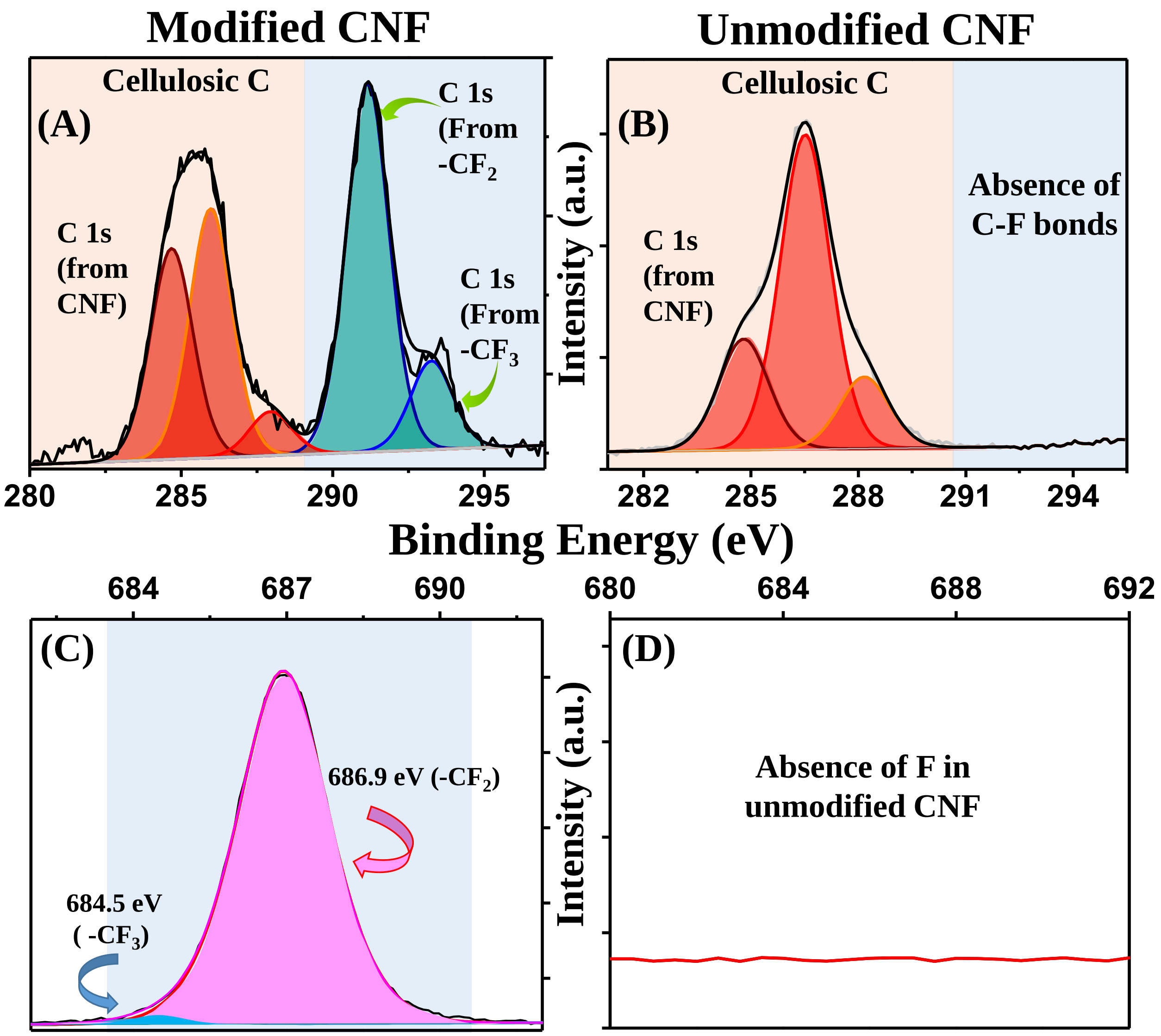


Figure 4.10 (A) Deconvoluted XPS spectrum in the C1s region of modified CNF showing the presence of carbons having different electronic environment. (B) Deconvoluted

XPS spectrum in the C1s region of native CNF showing the presence of only cellulosic carbons. (C) Deconvoluted XPS spectrum of F1s of the modified CNF. (D) Spectrum of the unmodified CNF. Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

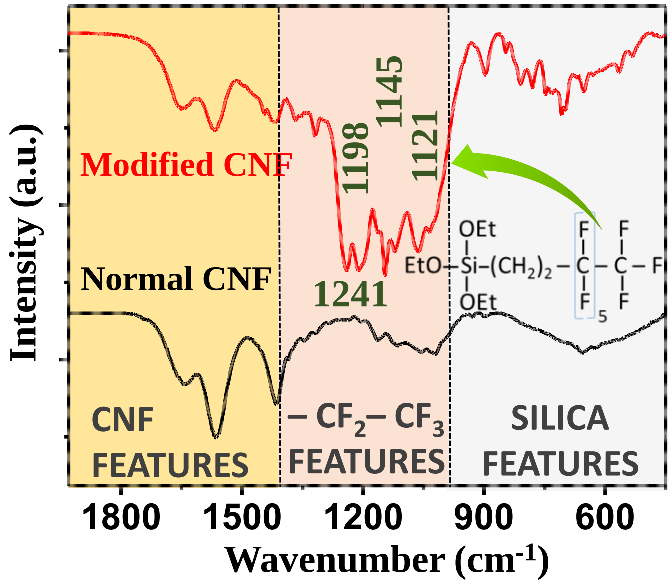


Figure 4.11 FT-IR spectra of the dried material (unmodified and modified CNF). Peaks at 1121, 1145, 1198 and 1241 cm^{-1} (shaded area) indicate the presence of C-F functionalities in the modified CNF. Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

The difference in IR spectral features (Figure 4.11) between modified and native CNFs also imply the change in its chemical signature. Observed characteristic peaks at 1121, 1145, 1198, and 1241 cm^{-1} in the modified CNF correspond to the various stretching modes of $-CF_2$ and $-CF_3$. New features at 1165 and 1130−1000 cm^{-1} correspond to different Si−O−C and Si−O−Si vibration modes, respectively. Therefore, microscopic and spectroscopic studies suggest that the unusual water repelling property of CNFs should arise from both enhanced roughness and low surface energy.

The self-cleaning property of the superhydrophobic surfaces has attracted people in various ways. This was demonstrated with iron oxide particles in the form of inorganic dust which eventually got washed away with rolling water droplets (Figure 4.12A−C). The coated paper when exposed to bacterial/fungal species showed no growth over its surface in spite of providing favorable conditions for growth. Even after prolonged incubation, the paper remained resistant to microbes. The observed color change around the unmodified CNF paper (Figure 4.12D) implies the growth of bacteria. For fungal contamination also, visible color change was seen unlike the coated paper

(Figure 4.12E). This microbial resistance is attributed to the water repelling nature of the coated surface. The coating prevented the access of the organisms to the nutrients and moisture needed for growth. Moreover, it has been seen that reduced protein adsorption plays an important role in reducing bacterial adhesion on surfaces (Zhang *et al.*, 2013). Chemical inertness or the stability of the modified CNF-coated surfaces were studied upon exposing the surface to organic solvents of different polarity such as hexane and ethanol (Figure 4.12F−H). Despite having porous morphology of the CNF film, which enhances the penetration and contact of organic solvents with fibers, characteristic superhydrophobic nature of the treated surface remains unchanged. This chemical robustness of the material was further studied and discussed later (Figure 4.13).

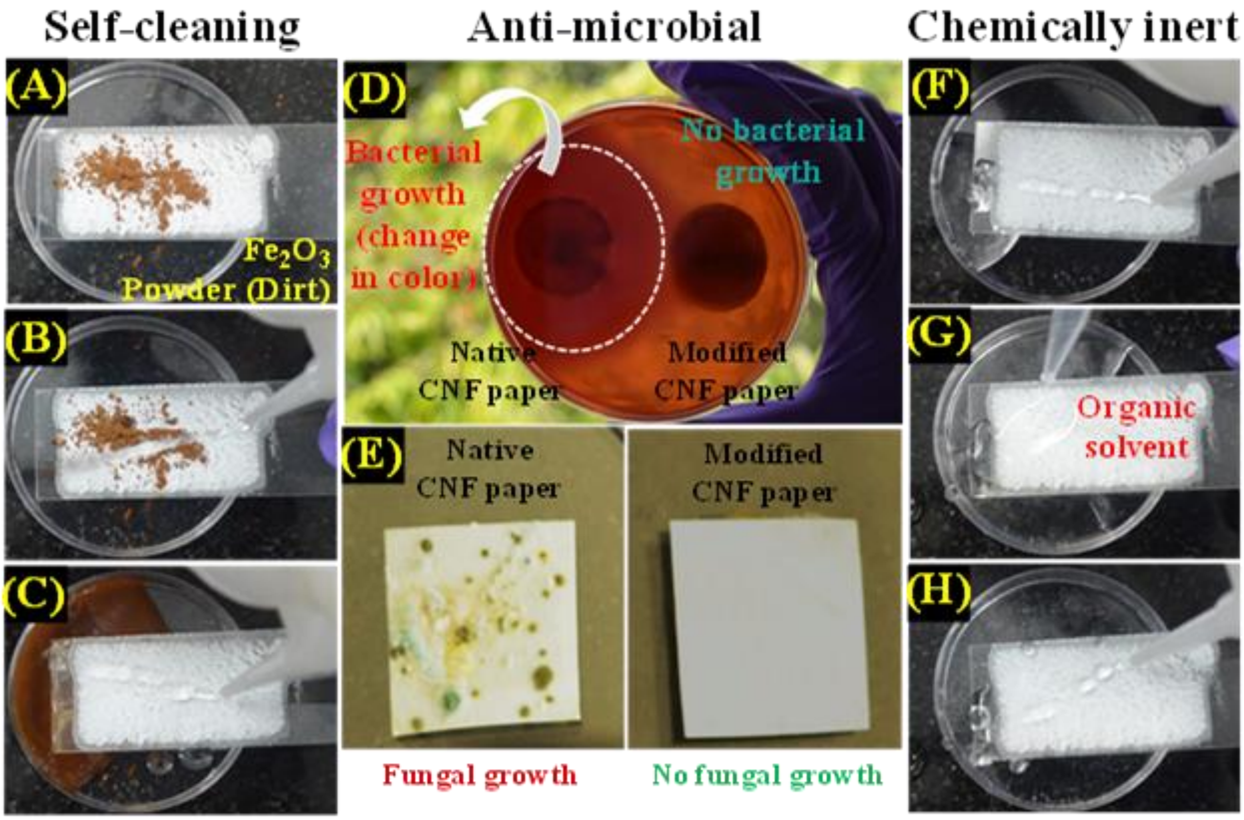


Figure 4.12 (A-C) Self-cleaning property of the superhydrophobic material coated glass surface. Iron oxide (Fe_2O_3) powder was used as the model dirt. (D, E) Microbe-resistive nature of modified CNF coated paper. Anti-bacterial (D) and anti-fungal (E) properties with native CNF paper as a reference sample. (F-H) Water-repelling behavior after artificially induced chemical damages with various organic solvents. Organic solvents having different polarities such as hexane and ethanol were used

to demonstrate the effect. Ethanol treated surface was used in photographs. Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

Though cellulose-based newly synthesized superhydrophobic material has shown significant resistance toward conventional mechanical and chemical stresses, the longevity of the material under various hazardous conditions is an important parameter for real-time applications in different technologies. This was tested in two different ways. In the first case, the same sample was kept in laboratory atmosphere and examined (by static CA measurements) for a long time (2 months) without applying any external stresses (Figure 4.13A). Second, the effect of different external perturbations such as exposure to various organic fluids (a diverse range of polarity), temperature, and direct sunlight was investigated in a cyclic fashion (Figure 4.13B). Details of the cycles are explained in detail in the Experimental Section (for each set of experiments, the same surface was used). For both of the cases, the wettability of the surfaces was studied by measuring the static CA of the water droplet. The consistent value of CA, on an average 160° (±2°), for both the experiments demonstrates the durability of the material for day to day applications.

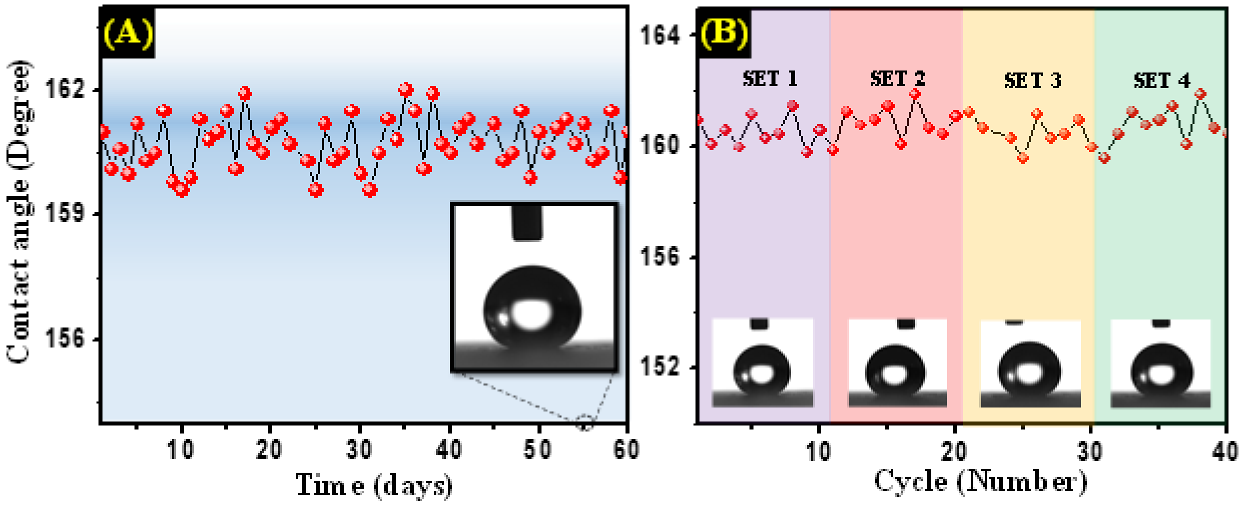


Figure 4.13 Durability of the coatings in (A) ambient condition (without any external perturbation) and (B) externally applied cyclic perturbations: (Set-1) exposure to various organic fluids, (Set-2) high temperature (200 ºC) treatment (Set-3) low temperature (-80 ºC) treatment and (Set-4) exposure to direct sunlight (longevity test). For both the cases (A&B), static CA of water droplet was measured at a regular time interval. (Inset) Photograph showing static CA of water droplet after

(A) 55 days and (B) each set of experiments. Details of the durability experiments are presented in the experimental section. Reprinted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

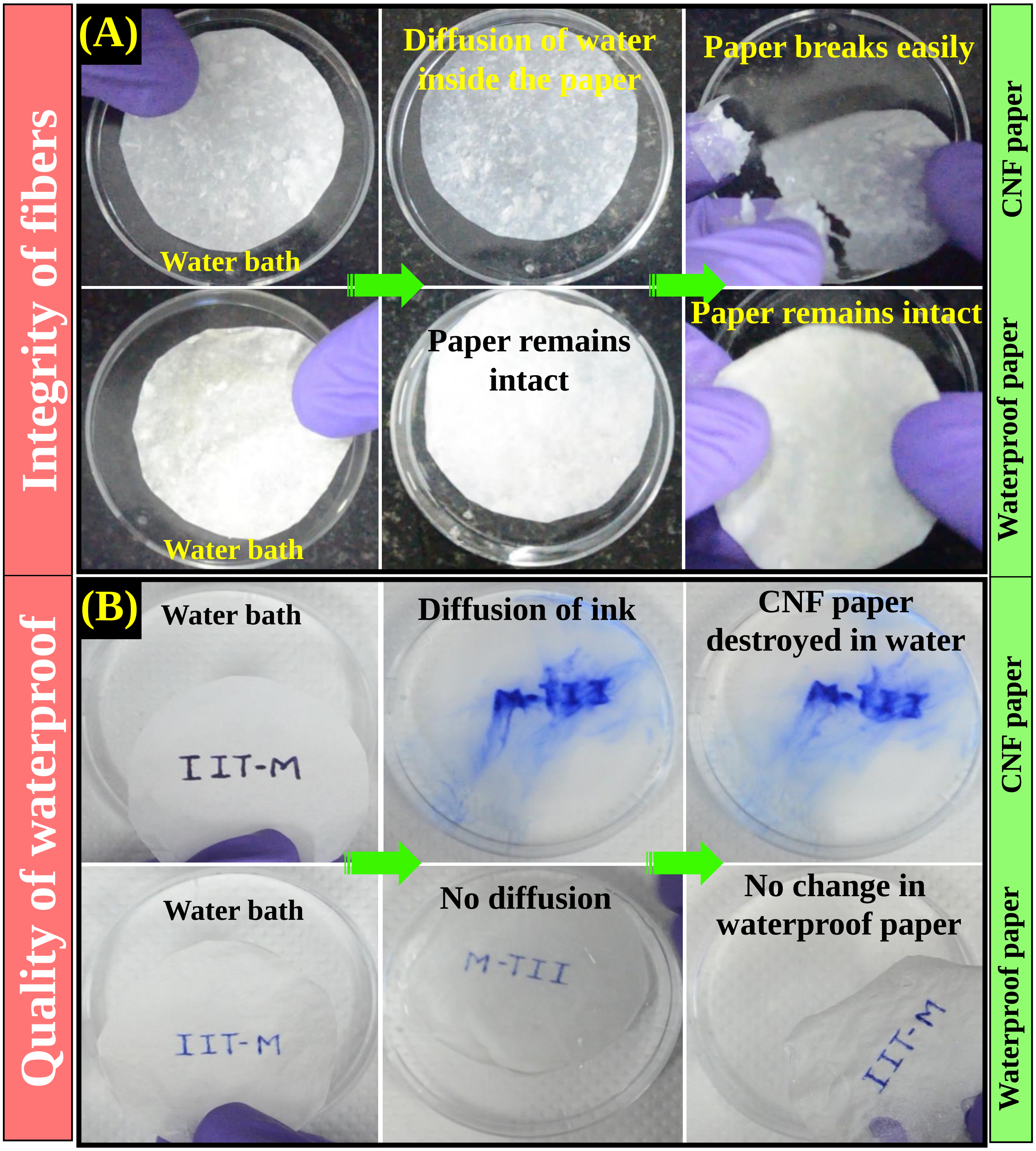


Figure 4.14 Key features of the prepared waterproof paper for paper-based technologies: (A) Integrity of the fibers upon exposing to water for a longer time (the waterproof

paper was compared with normal cellulose paper). (B) The extent of waterproof nature. Ink on the normal paper diffused as it came in contact with water whereas it remained intact on waterproof paper. Change in contrast of ink color is because of the uncontrollable soaking of ink in hydrophilic cellulose paper. Adapted with permission from publication I, (Baidya *et al.*, 2017) © 2017, American Chemical Society.

Being hydrophilic in nature, normal papers easily get wet through the diffusion (capillary action) of water, and this affects the integrity of the papers. In this context, waterproof paper with excellent resistance toward bacterial and fungal growth is advantageous for books, currency notes, medical diagnostic devices, and paper-based electronics. Proof of concept experiments have been performed as shown in Figure 4.14. A higher integrity factor for the modified CNF paper in comparison to normal CNF paper was observed when both the papers were put in a water bath for the same amount of time. The modified CNF paper was coated only on one side, and the same side was exposed to water during the experiment. Within a few minutes, normal CNF paper got wet and sank in the water (see the change in contrast). After 15 min of water treatment, while the normal CNF was destroyed by a small force, the modified CNF paper showed excellent resistance and remained intact (Figure 4.14A). In both of the cases, the forces were almost equal (neglecting the human error), which were applied manually. Furthermore, to show the quality of waterproof nature, native CNF and modified CNF-coated paper (single side coated) were tested with ink diffusion, where both the papers were written with blue ink (water-diffusible) and exposed to a water bath at the same time (ink written side was facing water). In this case also within a few seconds, the ink from the native CNF paper started diffusing in water, whereas the letters on the modified paper remained intact (Figure 3.14B).We believe that these important properties of the multifunctional waterproof paper will enhance the usability of such paper in paper-based technologies including flexible electronics as well as microfluidic devices.

4.4 Summary

In summary, we have demonstrated a simple strategy to develop a durable waterproof paper from chemically modified CNFs building blocks. Wettability of native hydrophilic CNFs was controlled through covalent linkages with low surface energy molecules in water. However, being synthesized and dispersed in water, this material also facilitates its applicability as an environmental friendly coating material for creating large area superhydrophobic surfaces. While the incorporated chemical functionalities enhanced the binding capability of the material with various substrates without any adhesive, physical appearance along with the mechanical flexibility of the waterproof paper remained unchanged, unlike the normal CNF paper. This material shows a durable water-resistant property which can withstand multicycle abrasion as well as chemical damages. Finally, chemical functionalization-induced enhancement of integrity (between the fibers) and excellent microbial resistance of the waterproof paper provide a basis for its applications in different paper-based technologies.

CHAPTER 5

Clay Based Robust Superhydrophobic Material Functioning both in Air and under Oil

5.1 Overview of Work

A fundamental challenge in artificially structured or chemically modified superhydrophobic surfaces is their poor chemical, mechanical and structural robustness towards different mechanical abrasions. This limits their application potential in different fields of science and technology. Herein, a stable waterborne superhydrophobic material composed of clay particles is developed through a one-pot chemical modification in ambient conditions, forming durable micro-nano dual-structured coatings at room temperature over a range of substrates, without adhesive (Figure 5.1). This chemical modification inverts the inherent hydrophilic nature of clay particles and provides an excellent superhydrophobic surface having a water contact angle>170°(±2°) and contact angle hysteresis<5°(±2°). The coating shows excellent durability against various induced damages (mechano-chemical-environmental) and works efficiently both in air and within oils. The observed property is due to the controlled surface energy obtained by the incorporated chemical functionalities and enhanced surface roughness facilitated by the hydrophobic-effect during slow evaporation of water from the coating material. Being a stable water-dispersion, it

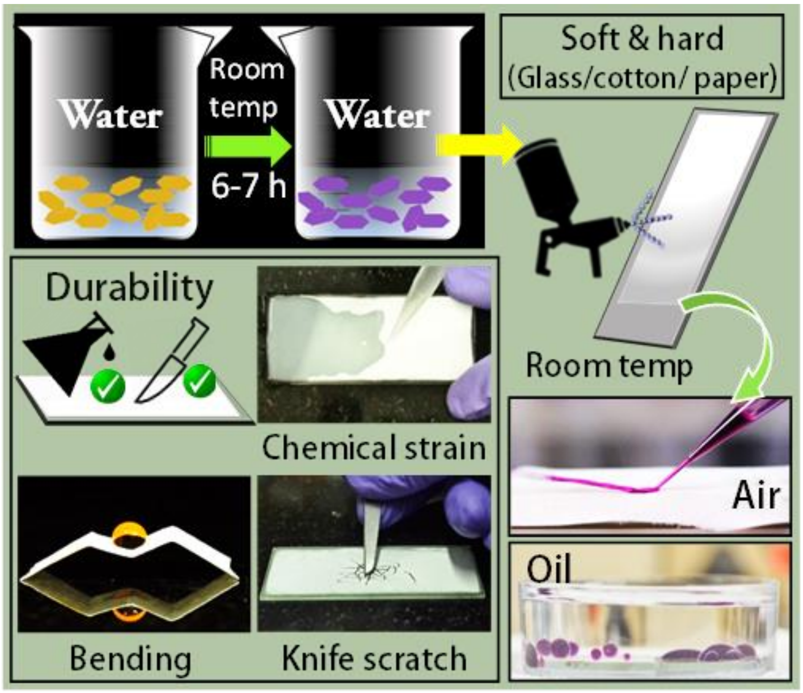


Figure 5.1 Schematic representation of the overall work. Reprinted with permission from publication II, (Baidya *et al.*, 2018) © 2018 John Wiley and Sons.

enables large area coatings, thereby minimising safety and environmental concerns. Use of this material to develop rugged waterproof-paper for various paper-based technologies is also demonstrated. As clay is commercially available and economical, we believe, this scalable organic-solvent-free superhydrophobic material will have a positive impact on various industries.

5.2 Introduction

Designing materials for the preparation of water repellent thin films with robust and durable characteristics has attracted considerable attention over the years because of their wide possible applications in different fields of science and engineering. However, one of the persistent problems of such chemically functionalised superhydrophobic surfaces is the poor stability and durability of the coating which readily gets abraded, for example even with the mild touch of tissue paper, leading to permanent loss of the surface property (Larmour *et al.*, 2007; Wen *et al.*, 2015; Tian *et al.*, 2016). Binding ability of the material with substrates having different surface morphology also affects the durability of the coating. To overcome these problems, although the use of adhesives and pre-surface modifications have been introduced (Lu *et al.*, 2015; Chen *et al.*, 2016), these methods have their own limitations depending on the nature of the adhesives and the surfaces to be coated. Nevertheless, the instability of such water repelling coatings towards various chemical stresses is still a major disadvantage. In this context, superamphiphobic surfaces, another class of materials were developed that repel both water and oil (Tuteja *et al.*, 2007; Tuteja *et al.*, 2008; Kota *et al.*, 2012; Zhou *et al.*, 2017). The surface energies of these surfaces are so low that they can maintain a thin layer of air between the surface and liquids which can subsequently result in rolling off of liquid. A few reports on the development of superhydrophobic surfaces (through chemically functionalized coating materials) that function equally well both in air and within oil are known (Chen *et al.*, 2016; Wang *et al.*, 2016). However, the use of hazardous organic/non-aqueous solvent systems and instability of the coatings without additives are the major limitations.

Fabrication of durable superhydrophobic fabrics with chemically processed materials is also a challenge despite having huge application potential of such flexible substrates in different paper-based technologies (Li *et al.*, 2016; Hou *et al.*, 2017). Fibrous surface morphology may prevent efficient coating which results in pinning/ sticking of water droplets on uncoated areas. Moreover, being soft and fibrous in structure, water droplets do not acquire enough energy or backward force to bounce off and get trapped within the fibrous microstructure.

In this study, a waterborne superhydrophobic material is developed from a hydrophilic clay particle building blocks that provides excellently durable superhydrophobic coatings at room temperature over a series of substrates (both soft and hard) without any adhesive. This demonstrates the novelty and possible industrial viability of the methodology. The material is environment-friendly, stable and can be made in large scale for different applications. Incorporated chemical functionalities controlled the surface energy of the material such that the coated substrate functions equally well, both in air and within oil. The coating showed excellent stability and unaltered water repelling property against various mechanical, chemical and environmental stresses. Being a water-based dispersion, it enables efficient and large area coatings by conventional coating procedures, thereby minimising environmental impact. Applicability of the material to develop a flexible waterproof paper is also demonstrated.

5.3 Results and Discussion

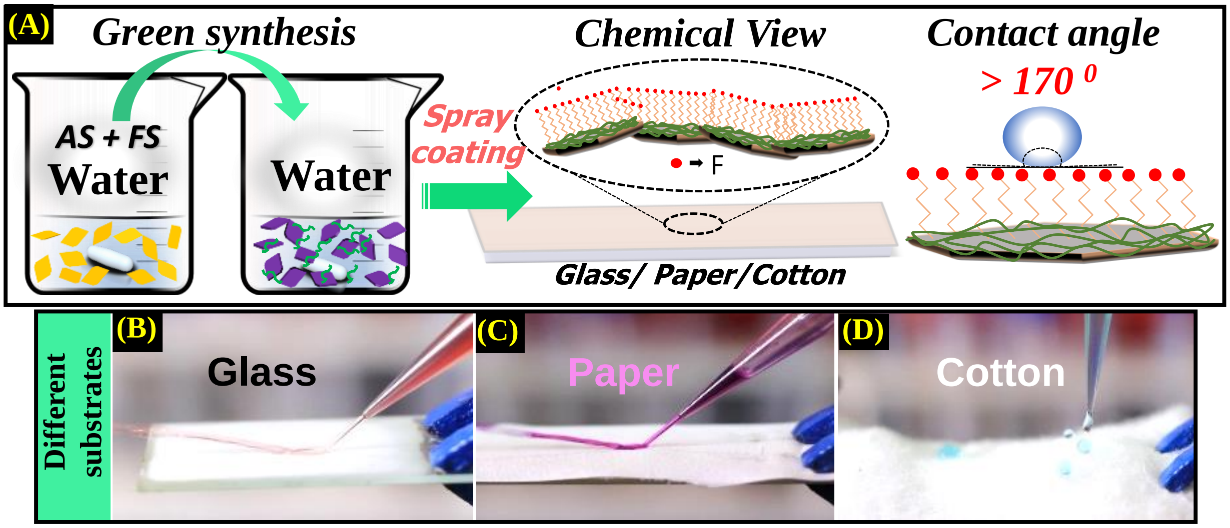


Figure 5.2 (A). Schematic representation of the waterborne superhydrophobic material (synthesis of the dispersion and the prepared thin film). Continuous jet flow on coated (B) glass, (C) filter paper and (D) bouncing of water on modified cotton surface. $KMnO_4$, $CoCl_2$ and $CuSO_4$ aqueous solutions were used in B, C and D,

respectively, instead of pure water to add color contrast. Reprinted with permission from publication II, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

Figure 5.2A illustrates the methodology used for the preparation of the superhydrophobic film over various substrates. Briefly, the complete reversal of the hydrophilic property of clay particles was achieved through a chemical functionalization with two different functional silanes, FS and AS in water at room temperature. Applicability of this waterborne material was tested both with hard and soft substrates such as glass, cotton, fabrics, *etc.*, having different morphologies. In addition to fluoroalkyl functionalization of the clay sheets, the surface has inherent micro and nano structures, as will be demonstrated later. It was seen that water droplets are spherical on superhydrophobic surfaces (both hard and soft) and bounce easily (Figure 5.2B-D). Moreover, bouncing off of water droplets even on modified cotton surface (Figure 5.2D) shows the universal applicability and efficiency of the material. Being dispersed in water, functionalized clay sheets sit readily on hydrophilic fibers and get coated efficiently all over the surface of cylindrical fibers by strong capillary action and large surface tension force (Chang *et al.*, 2016).

The extent of water repelling property of the material on fibrous soft surfaces was revealed from the unstable, frictionless movement of water drops on modified paper, demonstrated in Figure 4.3. This can be compared with the lotus leaf effect; a well-known example of the natural superhydrophobic property.

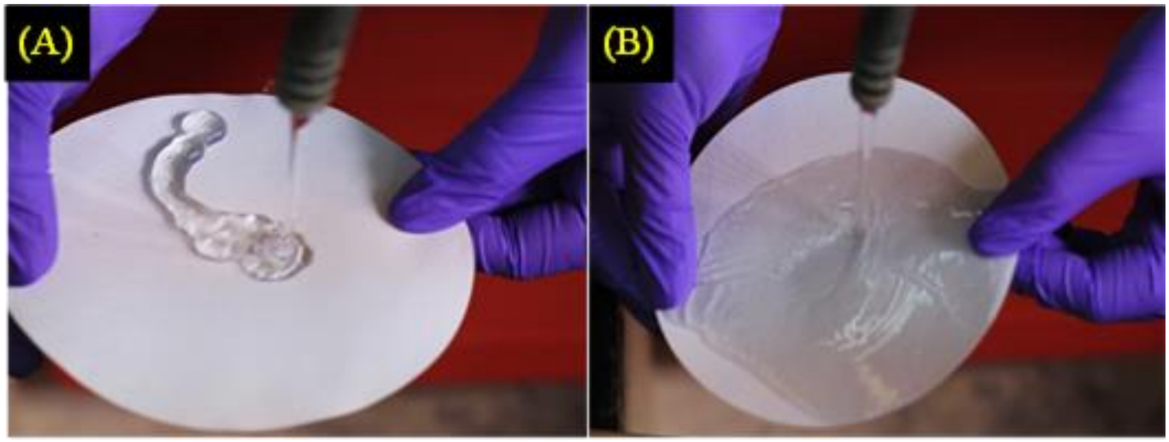


Figure 5.3 Water flows on (A) superhydrophobic material coated filter paper (Lotus leaf effect) and (B) normal filter paper. Water moves in a frictionless fashion on the coated surface whereas it wets the normal filter paper. Reprinted with permission from publication II, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

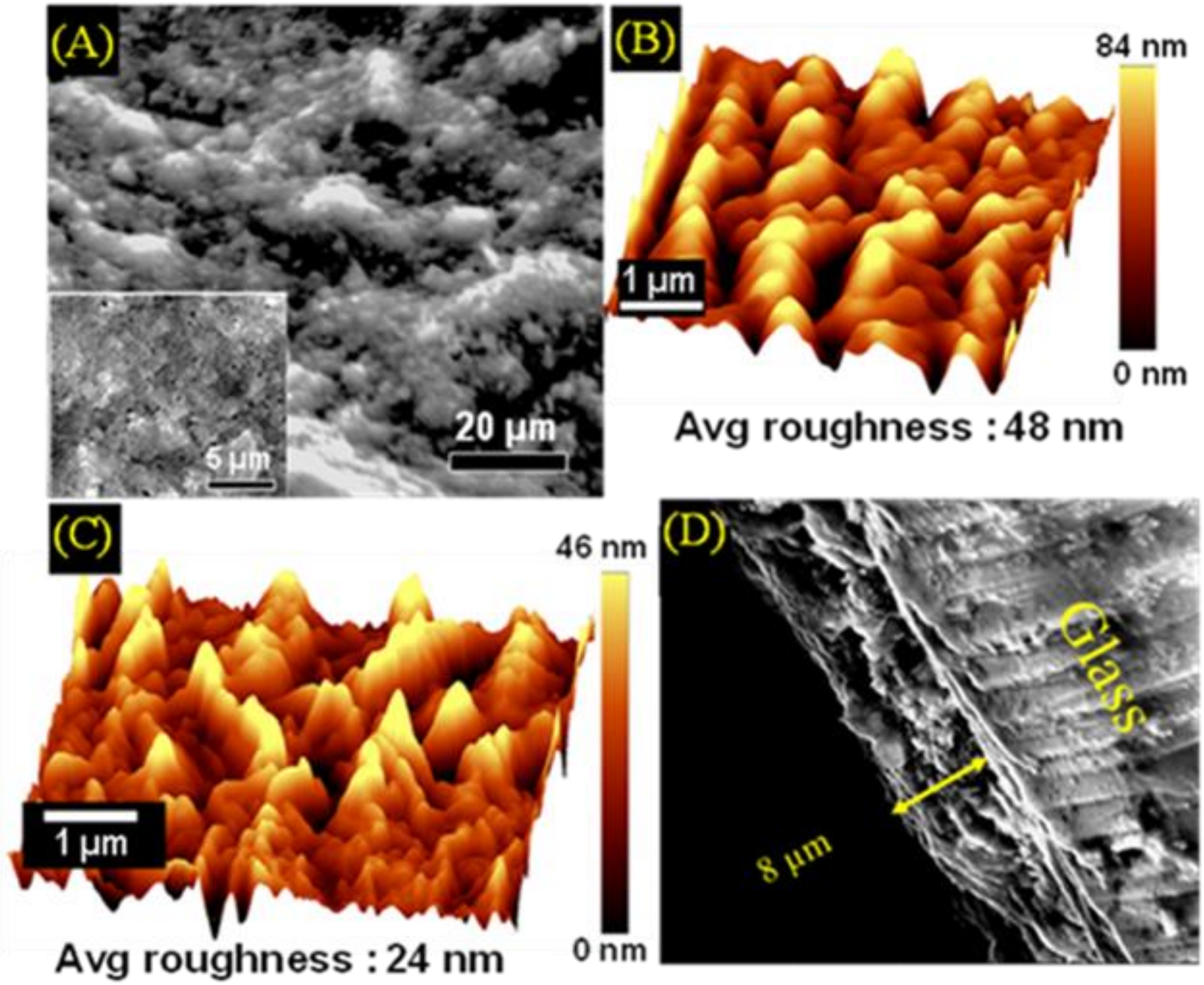


Figure 5.4 Characterization of the coating. (A) SEM image of coated glass substrate showing the uniform and periodic micronscale-features of the surface. The surface was tilted by 45º. Inset shows the morphology of the same surface at a tilt angle of 0º (B,C) AFM image of modified and unmodified clay coated surface showing different the nanoscale roughness present on the surface. (D) Cross-sectional SEM image shows the thinkness of the coating. Reprinted with permission from publication II, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

The surface morphology of the modified clay coated thin film (on glass) was imaged by scanning electron microscopy (SEM) with a tilt angle of 45º. The image (Figure 5.4A) manifests the periodic micron-sized features over the surface. Such features were observed throughout the surface and were formed during drying of the material at room temperature. While SEM showed micron scale surface structures, atomic force microscopy (AFM) revealed the enhancement of surface roughness in the nanometer regime (Figure 5.4B) as compared to a normal clay coated thin film (Figure 5.4C). In the case of a modified clay coated thin film, average surface roughness was 48 nm whereas it was 24 nm for normal clay coated thin film. This enhancement in roughness is related to the hydrophobic effect (Meyer *et al.*, 2006), namely an interaction between water and low surface energy molecules (here, fluorinated clay particles) that minimize the interaction energy and make the particles organize during drying of the aqueous coating. Such dual structured surfaces can be compared with nanopillar or nanograss surfaces as well (Shieh *et al.*, 2010). Figure 5.4D showed a cross-sectional SEM image of the superhydrophobic thin film suggesting a layer-by-layer structure of the coating.

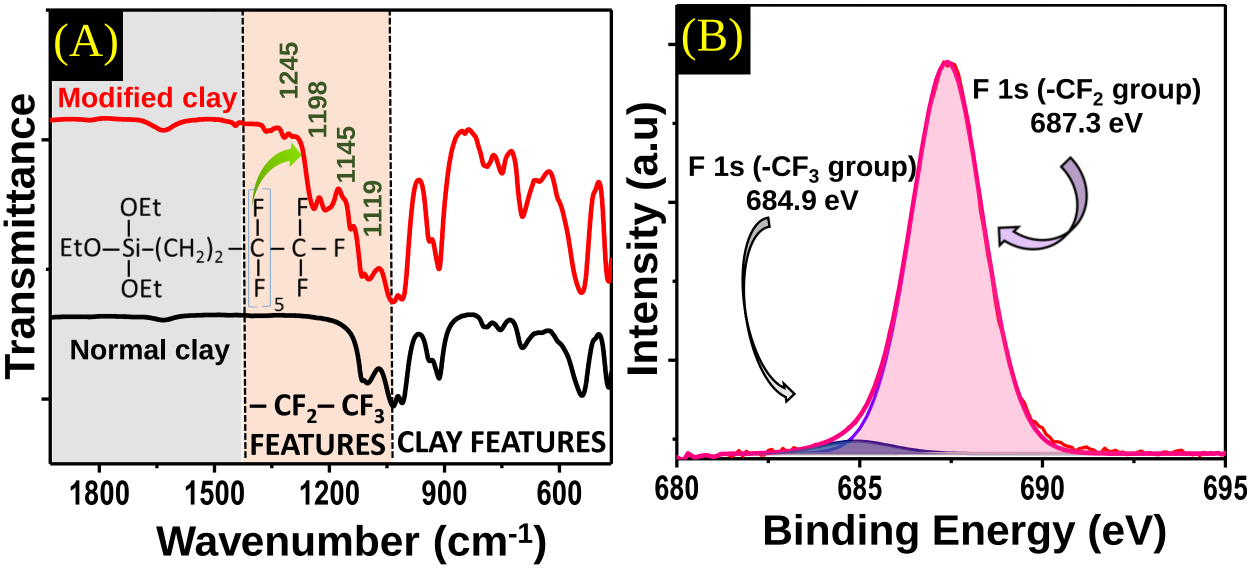


Figure 5.5 (A) FT-IR of the dried material. Peaks at 1119, 1145, 1198 and 1245 cm^{-1} (shaded area) indicate the presence of -C-F functionalities in the modified clay. (B) XPS shows the presence of fluorine in the sample which is coming from FS. Reprinted with permission from publication II, (Baidya *et al.*, 2018) © 2018 John Wiley and Sons.

Along with the surface morphology, chemical features of the surface also play an important role to obtain such extreme water repellent characteristics of the thin films. Infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS) reflect the chemical composition of the coated thin film. Figure 5.5A shows the IR spectra of unmodified clay and functionalized clay materials. Vibrational features are observed at 1119, 1145, 1198 and 1245 cm^{-1}, respectively, assigned to the stretching and bending modes of C-F bonds in FS (-CF_2 and -CF_3 functionalities). Intense peaks at 687.3 and 684.9 eV in the XPS spectrum correspond to the F1s of -CF_2 and -CF_3 groups, respectively of FS (Figure 5.5B). Both microscopic and spectroscopic measurements suggested the reasons of superhydrophobicity which are related to the surface roughness as well as the presence of low surface energy molecules.

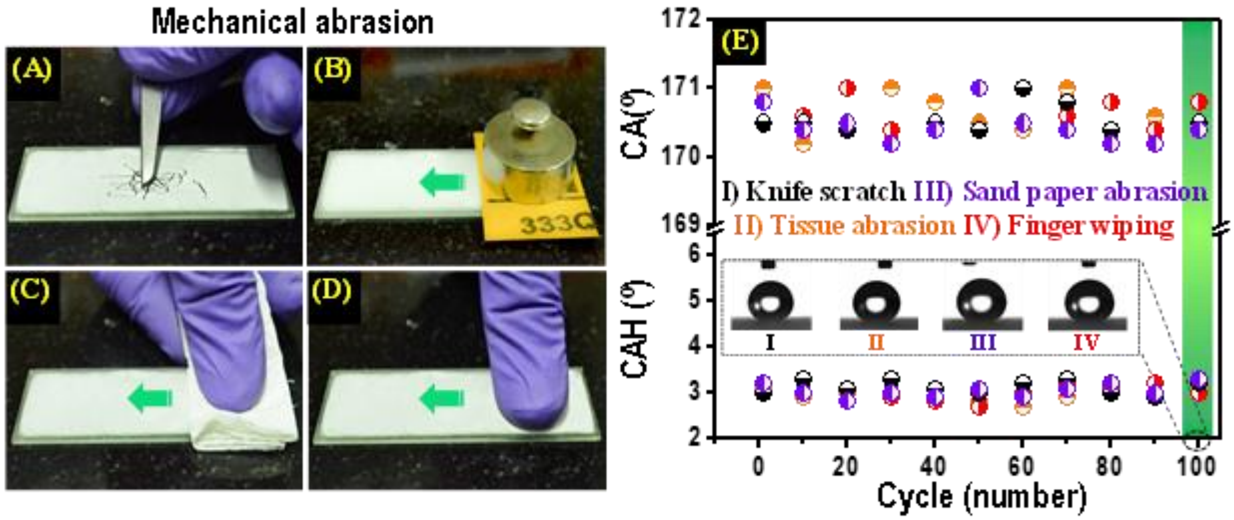


Figure 5.6 Induced hard and soft mechanical damages on spray-coated glass substrates. Hard mechanical damages: (A) scratching with a knife and (B) sand paper abrasion with 50 g of load. Soft mechanical damages: (C) abrasion with tissue paper and (D) finger wiping. (E) Durability/ longevity test with the above-mentioned mechanical tests. Change of CA and CAH of water droplet during the multiple abrasion cycles (of different mechanical tests). In every case, CA and CAH were measured after each experiment, consist of 10 consecutive abrasion cycles. (Inset) Photograph showing static contact angle of water on the tested surfaces (after the 9th experiment or 90th abrasion cycles). Reprinted with permission from publication II, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

Stability/durability of the coating is one of the most desired criteria when applications of such surfaces are concerned. In this context, use of additives to improve the strength and stability of superhydrophobic coatings has been reported which essentially enhances the binding ability of the coating material. In contrast, our material (without any adhesive) with diamino functional groups interlink the clay sheets and help to anchor them efficiently over substrates during the evaporation process through spontaneous in-situ polymerization. Anchoring induced stability was studied with various artificially induced mechanical stresses. For instance, the coated surface was subjected to hard mechanical stresses such as sandpaper abrasion test with a load of 50 g and knife scratch tests (Figure 5.6A,B). Although the coating on the surface got damaged to some extent with knife scratch, its superhydrophobic property remained intact. Interestingly, water repellent property was preserved for the sand paper abraded (with a load of 50 g) surface even after multiple abrasion cycles. These reflect the advantage of having multilayer surfaces, because even if the upper layers of the coating get affected, underlying layers can make the water to roll off (Verho *et al.*, 2011). Durability of the coating was also evaluated by soft mechanical stresses like tissue paper abrasion and finger wiping test (Figure 5.6C,D). In this case, abraded surfaces were observed to maintain their superhydrophobic property with easy movement of water streams over them. For all the cases, retention of the water repelling nature of the abraded surfaces was evaluated thoroughly with CA and CAH measurements after each experiment (Figure 5.6E) where each experiment consisted of 10 complete abrasion cycles of corresponding tests (details are given in chapter 3). Consistent values of CA and CAH at an average of 170° (±2°) and 3° (±2°), respectively, after each experiment showed the durability of the material against external forces. These mechanically perturbed surfaces were further studied with wettability sensitive vertical drop test (water droplet from the needle was moved vertically and contacted the surface and drawn back) and droplet drag test (water droplet from the needle was dragged over the surface back and forth for 5 cm). In all the cases, abraded surfaces were seen to retain their excellent water repelling characteristics intact. Unchanged wettability of these mechanically abraded surfaces are directly related with observed CAH (Figure 5.6E) of water droplets.

Having low surface energy, the coated glass surface showed self-cleaning property where graphite powder was used as dirt which eventually got washed away with the rolling water droplets (Figure 5.7A, B). Chemical robustness of this superhydrophobic surface was tested with various solvents with a wide range of polarities (ethanol, dimethyl sulfoxide, dimethylformamide, tetrahydrofuran, toluene, hexane, heptane and n-octane). For all the cases, coated surface was observed to retain its initial properties and remain unaffected after cyclic washing with multiple organic solvents, demonstrated in Figure 5.7C, D (ethanol treated surface is demonstrated here). Chemical durability of the material was further tested in detail with various hazardous aqueous solutions. For example, water with pH=1 & 14 and highly oxidizing KMnO4 solutions were used for this. Experiments were done in two ways. Firstly, these solutions were used directly to measure the static and dynamic contact angles of the respective droplets. In every case, the static contact angle was observed in the range of 170° (±2°) (Figure 5.7E-G) with low contact angle hysteresis, below 5° (±2°) (Figure 5.7I). This proves the stability and chemical inertness of the material. In the second case, the experimental solutions were used to wet the surface (similar to the experiment with organic solvents). However, in all the cases, their droplets bounced and rolled off easily over the surface. Durability of the coating under such chemical stresses was further tested by keeping the surfaces within the solvents for a long time (170 h for each solvent). For each solvent system, the same surface was used repeatedly for the entire experiment. After long incubation time also, surfaces retained their property and kept functioning efficiently. These were seen in the CA values at regular time intervals of 20 h for a duration of 7 days (Figure 5.7H).

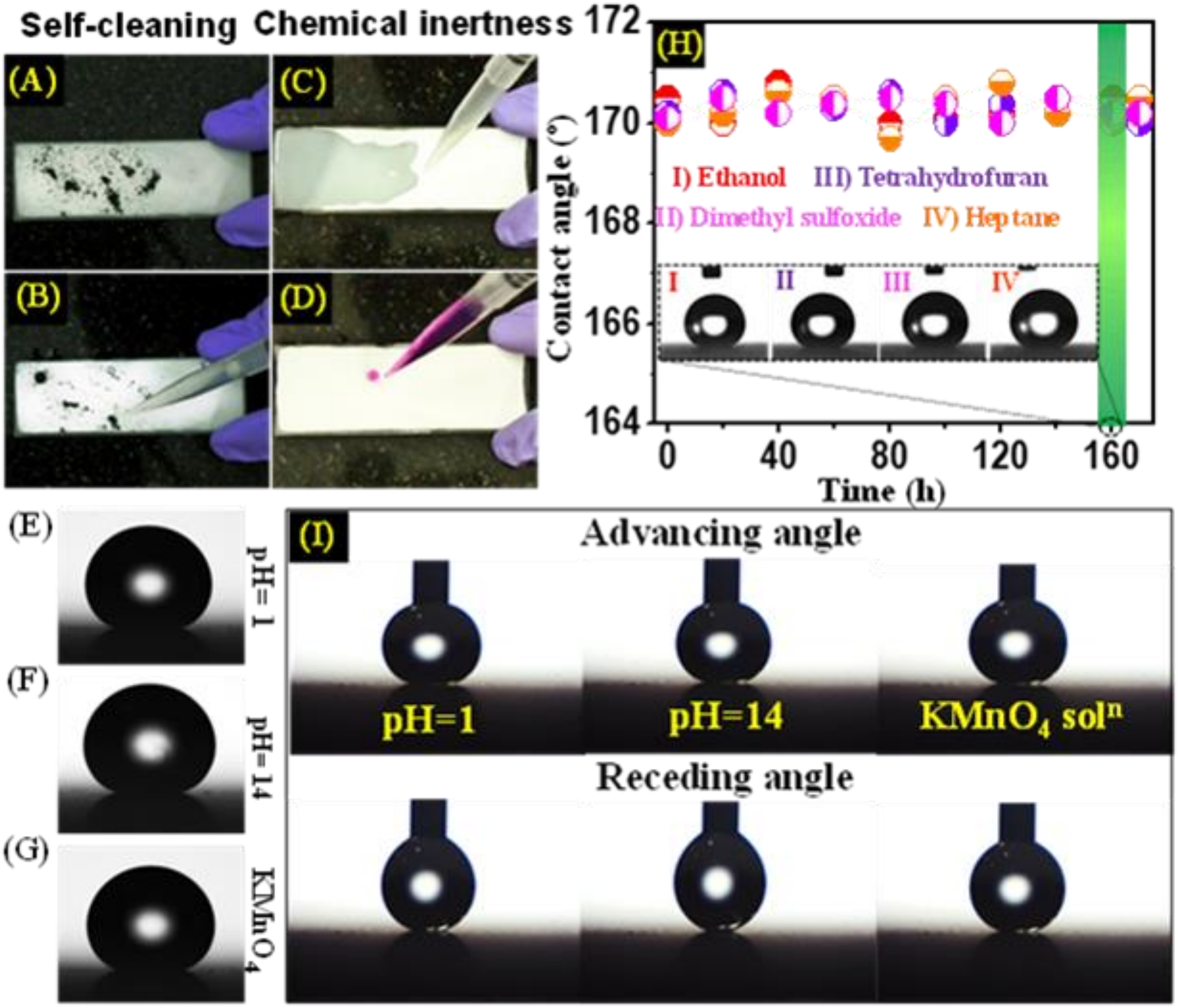


Figure 5.7 (A,B) Self-cleaning property of superhydrophobic material coated glass surface. Iron oxide powder (Fe2O3) was used as the model dirt. (C,D) Coated surface retains its water repelling behavior even after artificially induced chemical damages with

various organic solvents (ethanol treated surface is demonstrated here). (E-G) Static contact angle of water droplet having pH=1, 14 and oxidizing agent KMnO4. (H) Durability/ longevity of the coating under extreme hazardous conditions. Surfaces were kept inside various organic solvents having different polarity and the static contact angle of water droplet was measured after taking the surface out from the solvent in a regular time interval for 170 h (details in the experimental section). (Inset) Photograph showing static contact angle of water on a 160 h oil treated surface. (I) Contact angle hysteresis (CAH) of water droplets (pH=1, 14 and KMnO4 solution) over the coated glass substrates. Reprinted with permission from publication II, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

To identify the change in wettability of the superhydrophobic coating in detail, the treated (7 days solvent treated) surfaces were also studied by CAH measurements (Figure 5.8A), droplet drag and vertical drop experiments which are very sensitive towards surface wettability. Data corresponding to the THF treated surface are shown in Figure 5.8B (pictorially and graphically). Coated surface (paper, Whatman 44) was also observed to show bacterial resistance when it was exposed to bacterial species (Figure 5.9) under favorable growth conditions and nutrients. This was compared with normal paper where precipitation of bile salts around the uncoated paper indicates the bacterial growth.

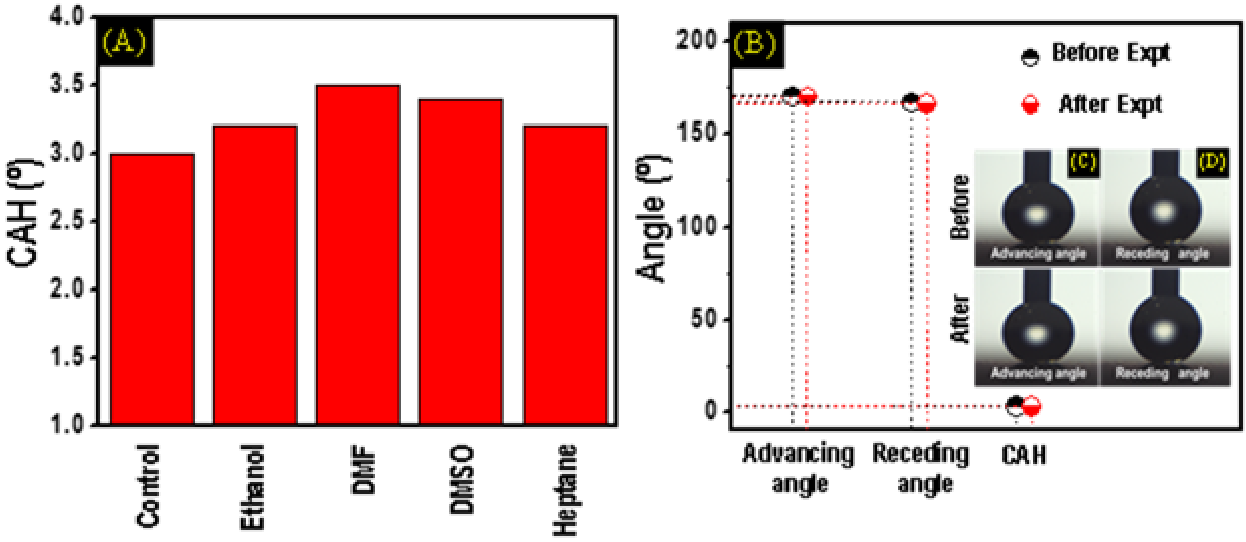


Figure 5.8 (A) Contact angle hysteresis (CAH) values of water droplet over 170 h chemically (different organic solvent) treated surface. (B) Graphical and pictorial representations of advancing angle, receding angle and CAH of water droplet over 170 h tetrahydrofuran (THF) treated surface (before and after). Images of (C) advancing angle and (D) receding angle (before and after). Experiments were done in air-water-solid interface. Reprinted with permission from publication II, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

Figure 5.9 Demonstration of bacterial resistance property of superhydro-phobic paper. This was compared with uncoated paper. Reprinted with permission from publication II, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

Oils, having low surface tension, easily get into the surface micro-structures and remove the air layer that is essential for superhydrophobicity. Water droplets possess lower interfacial tension inside oils compared to the air-water interface. Both of these enhance the possibility of pinning of water droplets on the surface. However, in our case, the superhydrophobic surface was observed to function also at the oil-solid interface with equal efficiency and maintains high static and dynamic contact angles for water droplets. A similar water repelling phenomenon at the oil-solid interface is well-known for SLIPS (Slippery Liquid-Infused Porous Surface), where low surface tension oils are introduced within a porous matrix (Smith *et al.*, 2013). In such cases, water droplets sit over these oil-wetted surfaces and remain surrounded by air. Whereas, in the present work, water droplet sits on a superhydrophobic surface and is surrounded by oil. Spherical shape of the colored water droplets on the superhydrophobic surface kept inside oil is pictorially presented in Figure 5.10A. Inset shows the measured static contact angle of the water drop inside n-octane which was observed to be 170° (±2°). Bouncing off of water droplets on the modified clay coated surface kept inside oil demonstrate the extent of under-oil superhydrophobicity. For laboratory experiments, non-polar long chain hydrocarbons (such as n-octane) were used as models for oil. Extent of such under-oil superhydrophobicity was further studied in detail with CAH measurements (Figure 5.10B) and vertical drop adhesion test inside oil (Figure 5.10C). In this case also CAH was observed to be 3° (±2°). Self-cleaning property of the surface when a portion of the surface was kept inside oil was also demonstrated with rolling water droplets (Figure 5.10D). Water droplets roll off easily through both the phases (air and oil) despite sudden change in the interfacial tension and kept the surface clean from dirt (potassium permanganate was used as a dirt).

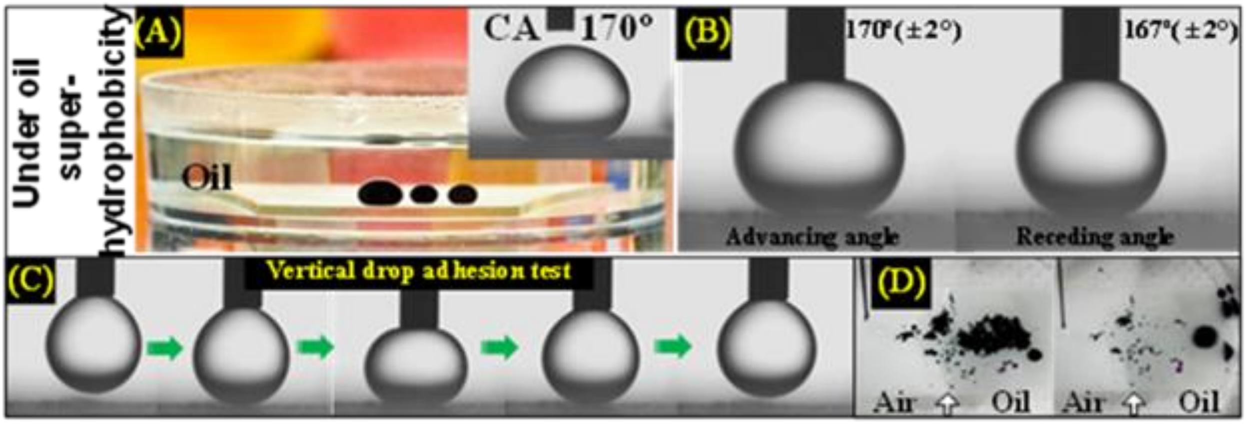


Figure 5.10 (A) The superhydrophobic coating also remained functional inside/under oil (n-octane) and forced water droplets to sit as a sphere whereas wetting takes place on a normal surface. (Inset) Static contact angle of water droplet on coated glass within the oil (n-octane). Extent of under-oil superhydrophobicity. (B) CAH measurement and (C) vertical drop adhesion test with a water droplet, when the coated surface was immersed in oil (n-octane). (D) Self-cleaning property of the coated surface at the air-solid-oil interface. A portion of the surface was kept inside oil (n-octane, taken as a model long chain hydrocarbon); an inorganic salt (potassium permanganate) was placed over it as a model of dirt. Rolling water droplets removed all the dirt from both the interfaces and made the surface clean. Reprinted with permission from publication II, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

To study the response of water repellent coatings against perturbed water droplets (as the interfacial tension of water droplets within oil is lower than in air and it takes time to reach equilibrium), coated surface was tested with droplet pinning test where the surface was kept inside oils with colored water droplets over it for a long time. Even after 1 h of incubation, droplets restored their spherical shape and started rolling upon mild shaking with hand. This can easily relate to previously demonstrated excellent under-oil superhydrophobicity (Figure 5.10). Figure 5.11A,B shows the displacement of these water droplets on the superhydrophobic surface kept under oil (initial and final positions of droplets are marked with colored circles). As the material functions well both in air-solid and oil-solid interfaces, it provides an easy cleaning strategy both for the surfaces (kept under oil) and oil. This is demonstrated in Figure 5.11C-E. While the dirt on the surface (under oil) can be collected with water drops and removed through capillary action (for paper) or mild shaking (induced force), small water drops in the oil can be removed easily by coalescing them on the superhydrophobic surface (kept under oil) followed by mild vibration/shaking. We believe that such a technique will be useful for oil pipelines and oil tankers.

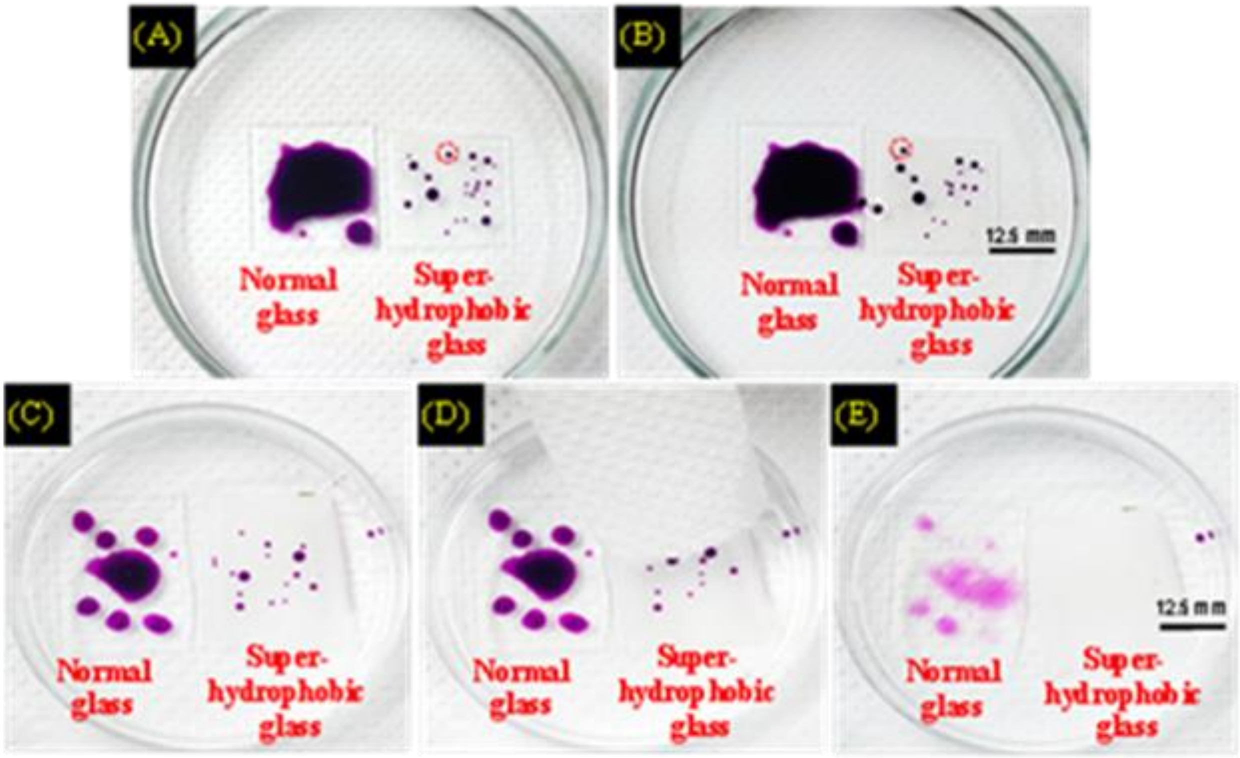


Figure 5.11 (A,B) Mobility of water droplets on oil immersed coated surface upon mild shaking with hand. Droplets were kept inside oil on the surface for an hour before the

experiment. $KMnO_4$ solution was used here for the visual effect. Colored water droplet moved by vibration with hand (initial (A) and final (B) positions are marked for two individual droplets with red and white circles, respectively). (C-E) Cleaning of water droplets from oil immersed coated surface; normal glass as a reference. Colored water droplets were wiped off completely from the superhydrophobic surface with tissue paper. (C) Before wiping, initial condition, (D) during wiping and (E) after wiping, final condition. Reprinted with permission from publication II, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

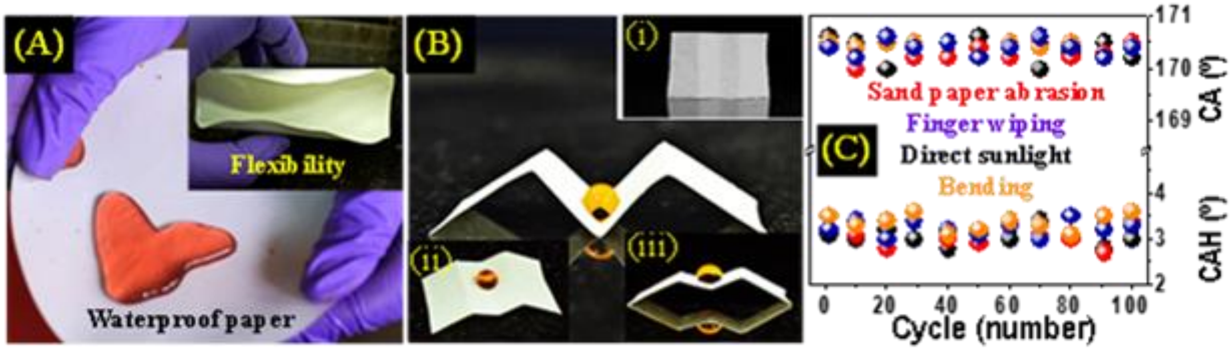


Figure 5.12 Demonstration of durability of waterproof paper. (A) Unstable water drops on coated filter paper (lotus leaf effect). Inset shows the retained mechanical flexibility of the paper after coating. (B) Induced twisting/ bending on the coated paper. Colored water drop on the folded paper that changed its shape to oval due to induced strain by the folded paper. Inset, i) vertical view of the folded paper after removal of water drop (after 10 mins). Any stain of the color drop was not observed. ii-iii) Water drop on relatively relaxed folded waterproof paper. (C) Durability/ longevity of waterproof paper under various mechanical and environmental stresses. Measured static CA and CAHs of water droplet after a regular time interval (details in the experimental section). Reprinted with permission from publication II, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

Being dispersed in water, these chemically modified clay sheets sit on fibrous materials efficiently through surface tension forces or strong capillary action and coat it efficiently without affecting the mechanical flexibility of the substrate. This was demonstrated with a coated filter paper (Whatman 44) shown in Figure 5.12A. Figure 5.12B pictorially represents the effect of bending/ twisting on the water-repelling nature of the coated paper. For this, a colored water droplet was placed on a strained folded paper that forced droplet to change its shape to oval. However, water repelling nature of the paper remains intact and no stain of the colored drop was observed even after 10 mins (Figure 5.12B i; folded paper was kept vertically). Droplet on the relatively relaxed folded paper is shown pictorially in Figure 5.12B (ii & iii; side and top views). Durability of this waterproof paper against various mechanical abrasions (sand paper abrasion and finger wiping test) and environmental stresses (effect of sunlight and effect of bending) was evaluated through static CA and CAH measurements in a cyclic fashion and the data are plotted in Figure 5.12C (details of the experiments were discussed in chapter 3). Retained superhydrophobicity of the coated paper under these conditions, a much desired property for various paper-based technologies, shows its applicability in day to day use.

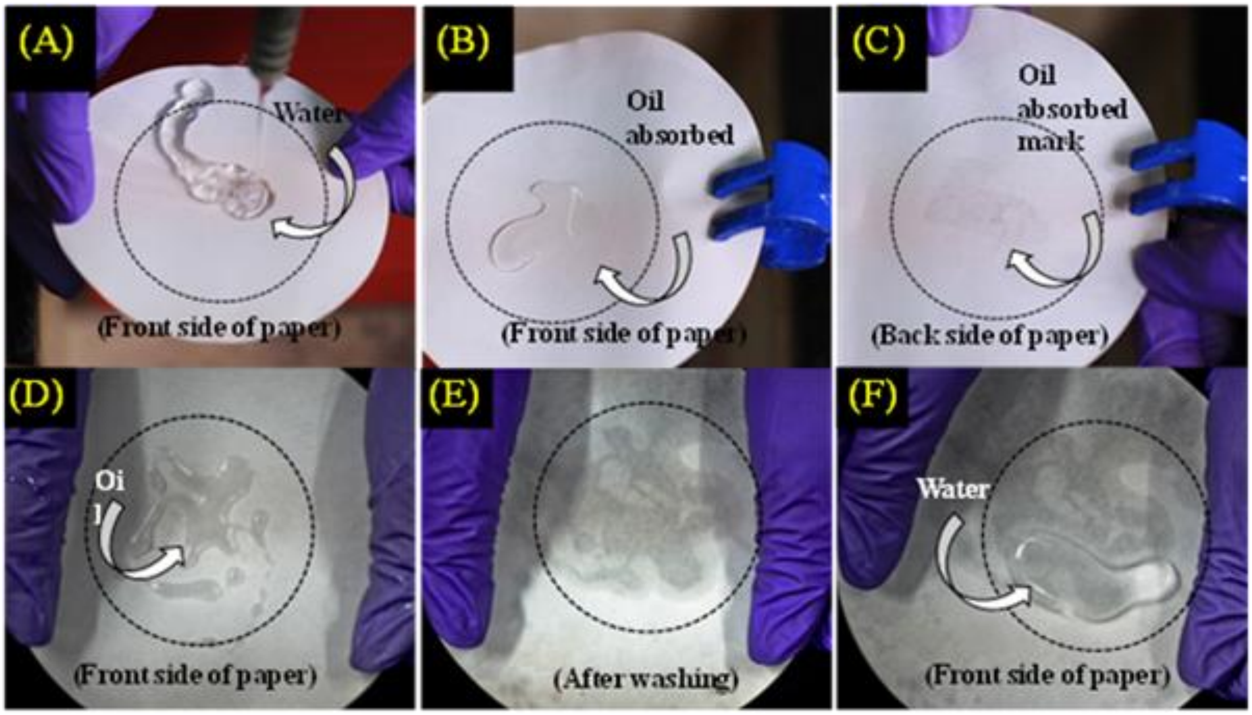


Figure 5.13 Demonstration of the superhydrophobic but oleophilic nature of flexible waterproof paper. (A) Unstable water drops on coated filter paper (lotus effect). (B-C) Paraffin oil on coated filter paper, part of which is absorbed by the paper (front side, B) and back side (C) of the same filter paper (with absorbed oil).Demonstration of durability of waterproof paper. (D-F) Oil washing test. (D) Paraffin oil adhering on the coated filter paper. (E) The same paper after washing thoroughly with acetone and ethanol to remove oil. (F) Washed paper shows almost similar water repelling

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The extent of binding of the material with fibrous substrates like filter paper (Whatman 44) was further demonstrated with a harsh oil washing experiment where viscous oil-absorbed coated paper was washed with organic solvents to remove the oil. Because of the superhydrophobic and oleophilic nature of the material, viscous paraffin oil absorbs over the coated paper easily as can be seen from the dark patches even on the opposite side of the paper (Figure 5.13A-C). These oil patches were subjected to multiple cleaning cycles with different organic solvents (ethanol and acetone). Though removing oil from the paper is difficult as it enters within the pores of the paper and gets immobilised on the fibers, interestingly, the washed filter paper showed almost equal water repelling nature (Figure 5.13D-F) and kept on functioning. This supported the excellent durability of the material as well as the developed waterproof paper.

Obtained excellent superhydrophic property along with the unique characteristics of the thin film can be explained with the chemical functionalities incorporated on clay particle along with the surface morphology of the film. Though the clay materials having silicate structure are hydrophilic, simultaneous functionalization with FS and AS inverts its physical property and induces durable water repellency once it is coated over surfaces (Figure 5.2). Firstly, anchored FS on the surface of clay sheets increases the hydrophobicity of the particles and facilitates the arrangement/orientation of chemically modified clay particles (keeping the fluorinated hydrocarbon chain outer side) during the evaporation of water. Such a process is mostly governed by the hydrophobic effect, namely an interaction between water and hydrophobic component of the dispersion. This also promotes the enhancement in the average roughness on the film which is much needed for superhydrophobicity. Secondly, the use of AS increases the dispersibility of the FS-modified clay particles. However, during the drying process, the amine groups mostly stays in the inner side (towards water) because of the same hydrophobic effect. Again, AS increases the strength, and durability of the superhydrophobic coating by connecting the functionalized clay sheets as well as anchoring them over the surfaces. As this polymerization is only observed/feasible upon evaporation of water, the water dispersed material stays unaffected until water is present. This helps in storing the material in closed conditions at room temperature for a period over a year without any special precautions. Finally, the decorated functionalities control the surface free energy of the film in such a way that the coated surfaces show equally efficient activity both in air and under oil. This was reflected in a high contact angle of 170° (±2°), with low hysteresis (below 5° ±2°) for water droplets both at air-solid as well as oil-solid interfaces.

5.4 Summary

In conclusion, we developed a versatile and simple waterborne composite material from hydrophilic clay particles building blocks that provides a durable superhydrophobic coating on large areas over a wide variety of substrates (without using any adhesive), having diverse surface morphology and physical characteristics. The material forms superhydrophobic thin films easily at room temperature that withstood various mechanical and chemical stresses. In particular, the surface showed excellent water repelling property even after 100 cycles of various mechanical abrasions such as sand paper abrasion, finger wiping, *etc.* Interestingly, the coated thin film functions equally well at both air-solid and oil-solid interfaces which is due to the controlled surface energy obtained by the incorporated chemical functionalities and hydrophobic effect-induced enhanced surface roughness during the slow evaporation of water from the coating material. Moreover, surface tension-induced better and effective binding capability of the clay sheets with soft and fibrous substrates makes it possible to design a flexible waterproof paper, a promising materials platform for paper-based technologies.

CHAPTER 6

An Aqueous Composition for Lubricant-Free, Transparent Slippery Coating

6.1 Overview of Work

Transparent durable coating materials that show excellent liquid repellency, both water and oil, have multiple applications in science and technology. In this perspective, herein, a simple aqueous chemical formulation is developed that provides a transparent slippery coating without any lubricating fluids, on various substrates extended over large areas (Figure 6.1). The coatings repel liquids having a range of polarity (solvents) as well as viscosity (oils and emulsions) and withstand mechanical strains. Exceptional optical transparency of 99% in the range of 350-900 nm, along with high stability even after cyclic temperature, frost, exposure to sunlight and corrosive liquids like aqua regia treatments make this material unique and widen its applicability in different fields. Besides, being a liquid, it can be coated on an array of substrates independent of their underlying topography, by various easily available techniques. Beside these interesting properties, the coating was demonstrated as a potential solution contributing to the remediation of one of the biggest global issues of tomorrow namely, affordable drinking water. Coated surface can capture 5 L of water per day per m^2 at 27 ºC when exposed to an atmosphere of 63% relative humidity.

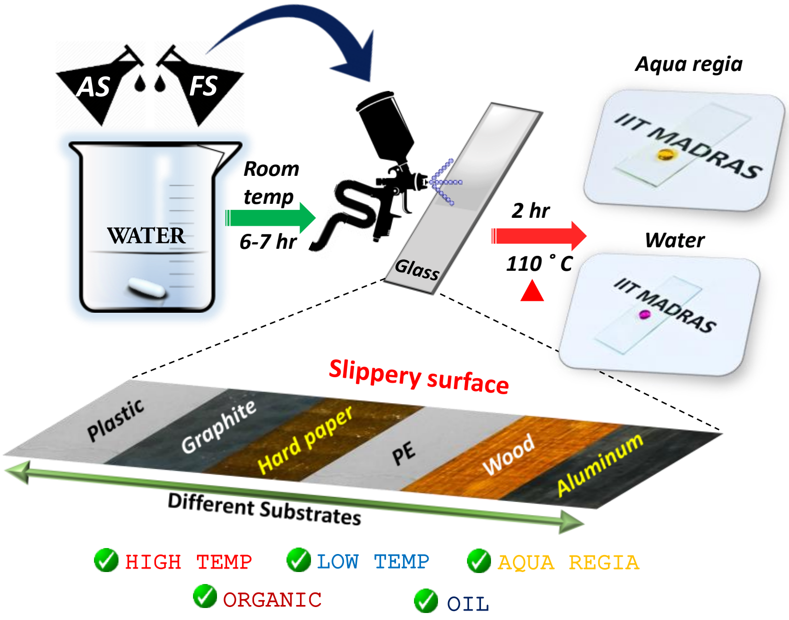


Figure 6.1 Schematic representation of the overall work. Reprinted with permission from publication III, (Baidya *et al.*, 2018) © 2018 John Wiley and Sons.

6.2 Introduction

Materials capable of imparting amphiphobic (hydrophobic and oleophobic) coatings are highly desirable for today's varied applications such as touch screen displays to glasses used in buildings, automobiles, *etc.*, and are being intensely researched upon. Although robustness towards chemical and mechanical stresses is one of the most needed/desired criteria of such coatings, high optical transparency has also drawn much attention of both industries and academia (Deng *et al.*, 2012; Lai *et al.*, 2012; Vogel *et al.*, 2013). Liquids usually have a high contact angle (CA) and a low contact angle hysteresis on these surfaces. In some cases, the surface energy of these coatings is so low that it makes liquids to bounce or roll over the surface and sit as a sphere, an effect known as superamphiphobicity (Tuteja *et al.*, 2007). While lotus leaf effect is the inspiration behind these developments, the trapped air in the micro-structured surface of lotus leaf is ineffective against liquids with low surface tension. To address this, recent research has come up with a 're-entrant surface curvature technology', a hierarchically developed surface structure with sufficient recess between the surface structure and its base causing liquids to sag below, without coming in contact with its sides or the base (Cao *et al.*, 2007; Tuteja *et al.*, 2008). These materials have ultra-low CAH and consequently high repellency for oils. However, the creation of these microstructures compromises the transparency (Cao *et al.*, 2008) of the material due to increased refractive index (Kobaku *et al.*, 2012; Kota *et al.*, 2012). Moreover, intricate micro fabrication technology needed to create such surfaces makes them rather expensive and in addition offer limited surface compatibility. Furthermore, high CA leading to lower contact area between the liquid drops and these surfaces makes it difficult to accomplish various industrially significant features including heat transfer, condensation and many others (Chandra *et al.*, 1996; Rosengarten *et al.*, 2006). In this context, SLIPS (Slippery Liquid-Infused Porous Surfaces), with equally efficient liquid repellent property, known to possess low CA and low CAH while allowing high contact area, is an alternative (Solomon *et al.*, 2017). *Nepenthes pitcher*-plant inspired surfaces of this kind were developed by infusing low surface tension liquids, such as perflurinated oils, inside the nano/ micro structured porous matrices (Smith *et al.*, 2013; Chen *et al.*, 2014). Recently, Chen and co-workers have reported a cellulose based transparent slippery surface that repels both liquids and ice (Chen *et al.*, 2014). Kang and co-workers have developed transparent hydrophobic electrodes in the context of outdoor solar cell devices where non-wetting property keep the surface clean and allows efficient/effective absorption of sunlight (Kang *et al.*, 2017). Furthermore, such water repelling surfaces having large contact area of water droplets are more efficient for condensation based technologies like water/humidity harvesting that can help to solve the water scarcity. In this context, Kim and co-workers have developed a graphene based hydrophobic surface (Kim *et al.*, 2014). However, large scale production of such surfaces can be an issue and expensive as it was obtained at very high temperatures (~1000 °C) through in-situ chemical-vapor-deposition. Therefore, designing a simple coating material to develop an affordable and scalable liquid repelling surface (both for water and for other liquids) devoid of lubricating fluids with durability is important. Incorporation of transparency can also explore the applications of such surfaces towards different global issues including energy crisis.

In the context of transparent water repelling coating, use of polydimethylsiloxane (PDMS), a widely used hydrophobic coating material, also gets limited attention because of its solvent (organic) and substrate (except glass) compatibility. It also possesses inherent limitation in transparency when exposed to different temperatures. This suggests the necessity to develop a coating material in water that can provide a robust liquid repellent slippery coating over various substrates, irrespective of their shape, size and surface morphology.

In this work, we present a novel waterborne material which is a liquid at room temperature and shows excellent liquid repellent property (without any lubricating fluids) upon curing over the surface. The material can be painted or coated as a thin film on various substrates like metal, glass, hard plastic, paper, *etc.*, despite their varying surface morphology. Being a liquid, large area coating by processes like spray coating, spin coating and doctor blading are possible which widen its applicability. Coated substrates show excellent liquid repellency with 99% transparency when compared to clean room treated glass slides. Interestingly, coating withstands various thermo-mechano-chemical damages without any adhesives and retains its properties intact. We believe, a combination of reduced surface energy along with rigid nanoscale structures, which form during the rapid polymerization process, help these coatings to repel a wide variety of liquids irrespective of their polarity and viscosity. Beside these multiple effective properties, applicability of this coating for efficient water condensation is demonstrated as a proof of concept for atmospheric water capture that can resolve one of the biggest global issues namely, the water crisis.

6.3 Results and Discussion

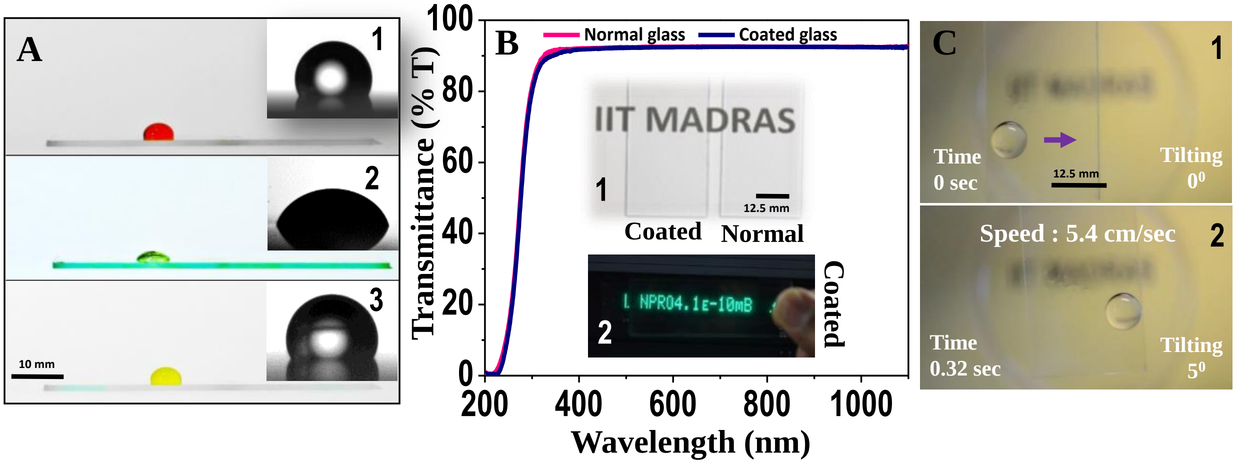


Figure 6.2 (A). Photographs of the coated surface with different liquids; 1-Water, 2- Toluene, 3- Aqua regia. Inset, the static contact angle of the respective liquids. (B). Percentage transmission of coated glass in comparison to a normal glass. The coated surface showed 99% transmission when compared to the normal uncoated surface. 1. Coated surface just before the written letters. 2. Electronic letters through the coated surface (distance: 8-9 cm approximately). (C). Image shows that at low tilting angle (5˚) of the coated surface water slipped off at a speed of 5.4 cm/sec. Reprinted with permission from publication III, (Baidya *et al.*, 2018) © 2018 John Wiley and Sons.

Figure 6.2A demonstrates that a wide variety of liquids from water to toluene and even corrosive acids such as aqua regia sit over the coated surface without spreading. This indicates low surface free energy of the coating which was investigated further. Inset shows the static contact angle (CA) of those respective fluids over the surface. Exceptionally high optical transparency of the coated glass was observed using UV-Vis spectrometry (Figure 6.2B). About 99% transmission in comparison to clean room-treated glass is shown in Figure 6.2B, inset-1&2. No observable differences in the visibility were found even when the coated surfaces were tested in front of an electronic display, approximately 8-10 cm away from the surface Figure 5.2B, inset-2. Initially, the wetting property of the coated surface was tested with the movement of the water drop (~100 μL) on the surface when it was tilted manually for a few degrees (details are in the experimental section). The velocity of the slipped water drop was measured as 5.4 cm/sec (Figure 6.2C). Such a property of the coating resembles the slippery surfaces and was further studied in detail later on. This phenomenon can lead to a range of applications in energy reduction, in the context of liquid transport.

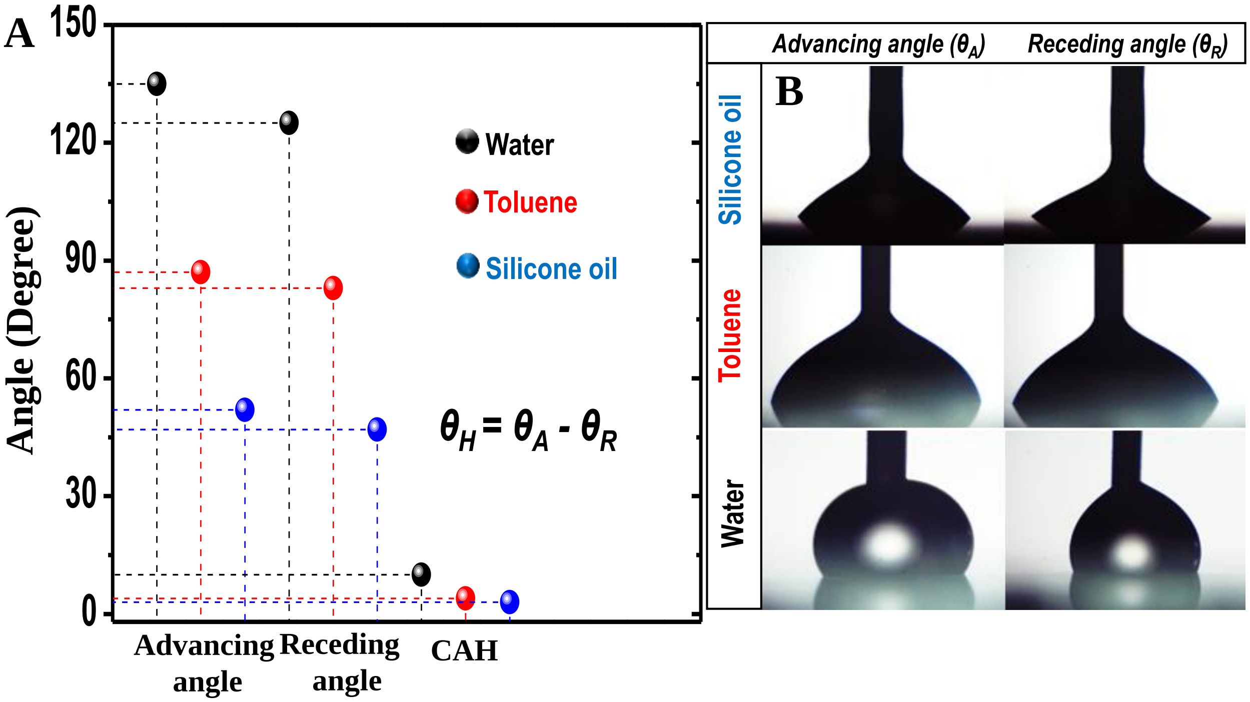
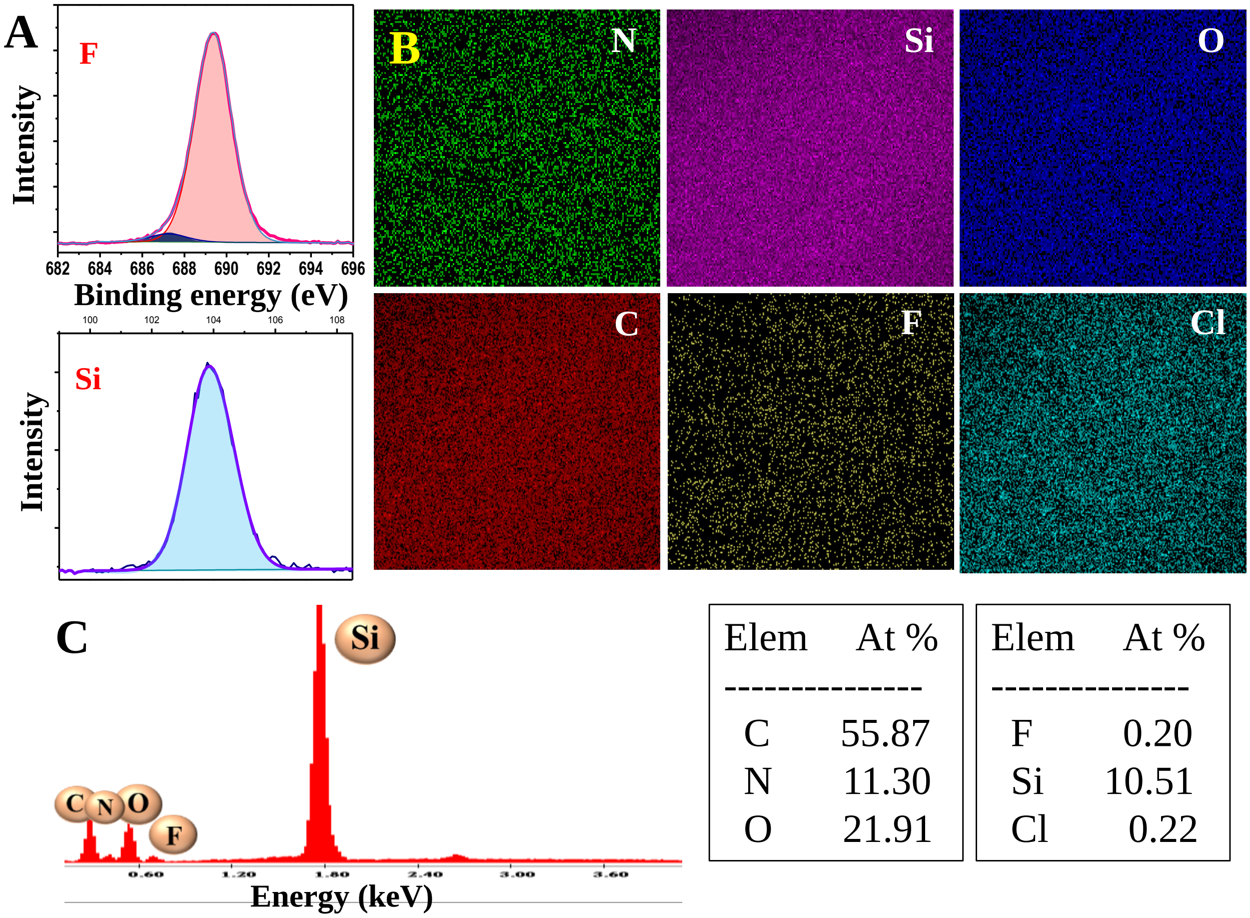


Figure 6.3 (A) The advancing angle (θ_A), Receding angle (θ_R) and contact angle hysteresis (θ_H) of water, toluene and silicone oil, respectively. (B) Corresponding images of advancing angle (θ_A), Receding angle (θ_R) for respective fluids. Reprinted with permission from publication III, (Baidya *et al.*, 2018) © 2018 John Wiley and Sons.

Low surface tension liquids (like oils and emulsions) usually wet the surface and spread easily. Here, the wetting behaviors of the coated surface towards various liquids having different surface tensions were assessed by both static and dynamic CA measurements where dynamic CA is represented in terms of CAH. For instance, water droplet placed on the coated surface formed a static contact angle of 134±2°; whereas, for toluene and silicone oil, it was 86±2° and 52±2°, respectively (Figure 6.3A). It correlates with the surface tensions of the respective liquids. However, low CAH in the range of 10±2°, 4±2° and 3±2° for water, toluene and silicone oil, respectively, reveal the extent of the slippery nature of the coating toward different liquids despite having low static contact angle on the coated surface (Figure 6.3A). Advancing and receding angles of the respective fluids are pictorially presented in Figure 6.3B.



Elem	At %
C	55.87
N	11.30
O	21.91

Elem	At %
F	0.20
Si	10.51
Cl	0.22

Figure 6.4 (A) The XPS spectra of the coated surface showing fluorine 1s and silicon 2p region. (B) SEM EDAX mapping and quantitative distribution of elements. (C) EDAX spectrum shows the elemental composition of the coating. Reprinted with permission from publication III, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

Surface structure and the chemical composition, being the underlying reasons of the wetting property, the coated surface was characterized in detail through various spectroscopic and microscopic techniques. XPS spectra reveal that the coating is largely composed of silica and fluorocarbons (Figure 6.4A). Peak at in the region of 103.5 eV corresponds to the deconvoluted Si 3p peak of Si^{4+} which matches exactly with that of silica (SiO_2). The presence of silicon, nitrogen and other elements along with fluorine was proved from the EDAX spectrum and mapping as well (Figure 6.4B,C). Wide area powder X-ray diffraction of the film showed an amorphous background, similar to the glass substrate (Figure 6.5A). This was also observed in the qualitative elemental distribution of silicon and oxygen (1:2) in the EDAX mapping of the surface (Figure

6.4C). These detailed chemical characterization concludes that the back bone of the coating is made of silica network. This was also reflected in the robustness of the coating towards thermo-mechano-chemical perturbation, explained later on. Though SEM reveals the absence of micron scale structure (Figure 6.5B), AFM imaging confirms that the roughness of the coatings is very low, less than 1 nm (Figure 6.5C,D). Both of these studies (spectroscopic and microscopic) suggest that the nano-structuring and the presence of appropriate functionalization are the reasons of this observed wetting property.

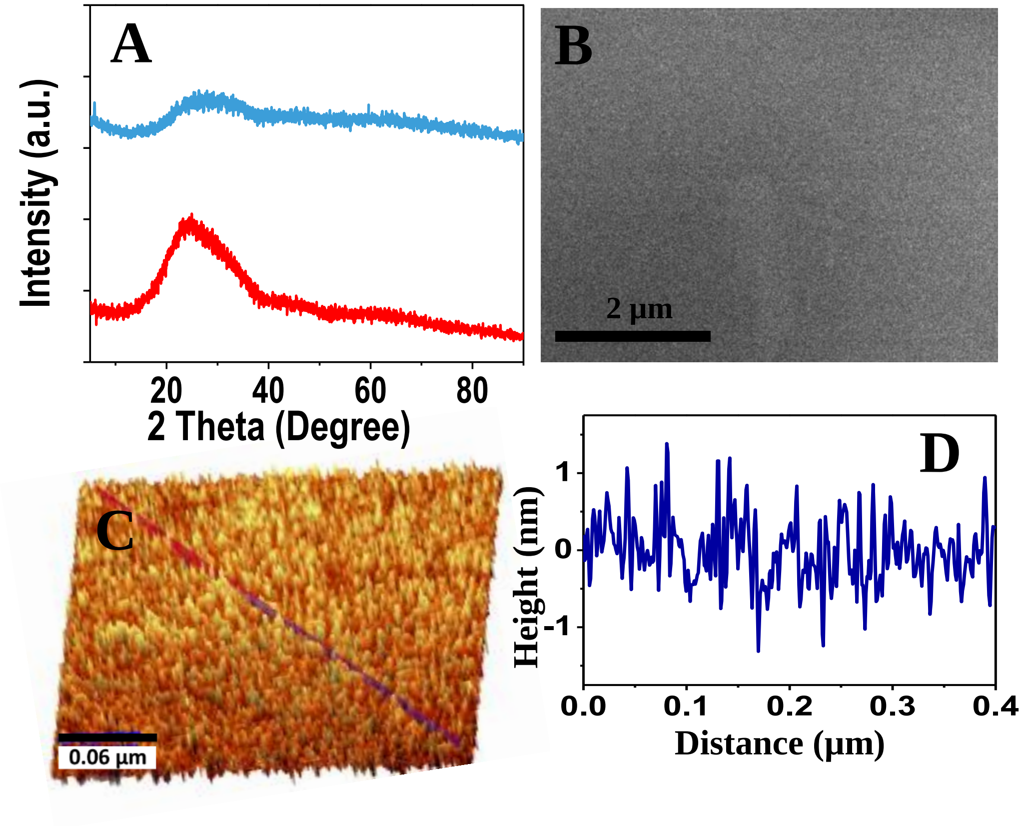


Figure 6.5 (A) Powder XRD: Amorphous structure of glass is unchanged with coating. (B) SEM image reveals the absence of micron scale morphology. (C, D) AFM image and the average roughness of the coating which is in nm scale. Reprinted with permission from publication III, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

To demonstrate the extent of water repellency of the coating material, a glass slide was coated in the shape of ‘⊟’ consisting of 2 uncoated patches in the middle (Figure 6.6). The hydrophobic coating in the periphery of the glass slides acted as an invisible barrier to contain approximately 4 ml of water in the uncoated hydrophilic patches having a surface area of 7.8 cm^2. As a result of this confinement, the water could reach a height of 0.4 cm in each of the patches (Figure 6.6). This concept of the invisible barrier has been used by others too and can be used in trapping, directing as well as retaining water and can have immediate applications in biological and environmental areas.

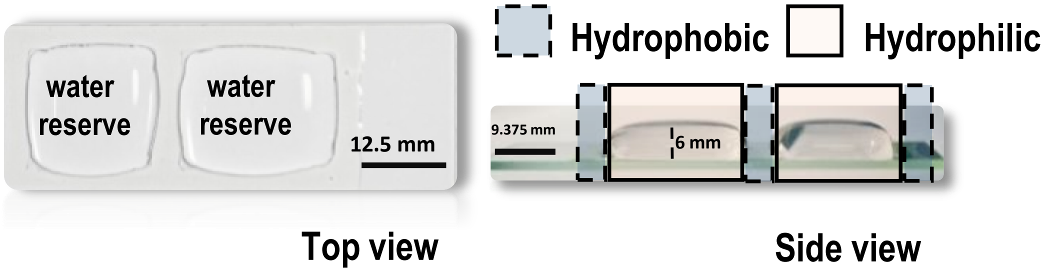


Figure 6.6 Designed invisible water barrier holds up to 4 mm height of water in air. The top and side view of the water mountain. Reprinted with permission from publication III, (Baidya *et al.*, 2018) © 2018 John Wiley and Sons.

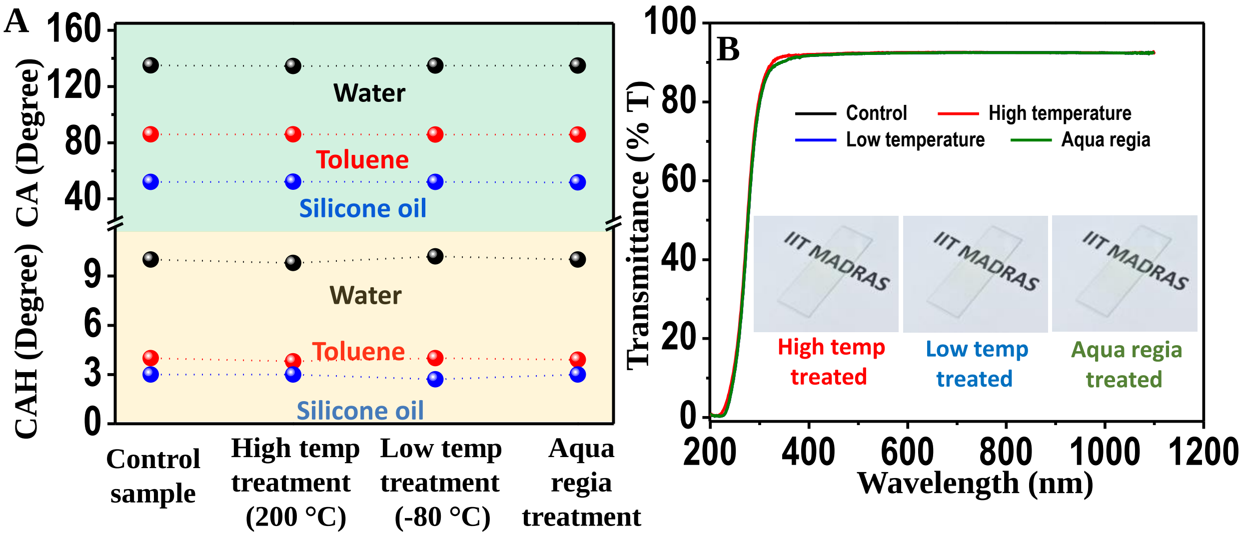


Figure 6.7 (A). Stability of the coating upon high temperature (200 ºC), low temperature (-80 ºC) and aqua regia treatments. CA and CAH of the liquids (water, toluene and silicone oil) on the treated surfaces compared to the control. (B). Corresponding percentage transmission of the treated substrates shows no change in comparison to the control. Inset, pictorial representation of treated surfaces. Reprinted with permission from publication III, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

For applications in touch screens, goggles and windscreens, the coating needs to be resistant to acute temperature fluctuations and chemical disruptions without compromising transparency of the surface. The stability and wettability of the coating against thermal and chemical damages were evaluated with extreme temperatures (high and low) and aqua regia (corrosive acid mixture). For all the cases, water, toluene and silicone oil were used to study the wettability of the treated surfaces in terms of static CA and CAH. Glass substrates were assessed primarily to monitor the transparency and integrity of the coating. For high temperature treatment, surface was annealed at 200°C for 4 h and it was observed to retain its surface free energy intact compared to the control sample (coated slides at room temperature). This was reflected in the CA and CAH of the liquids over the treated surface (Figure 6.7A). The stability of the coating at low temperatures was tested by incubating the surface at -80°C for 8 h. In this case, a similar liquid repellent property was observed for the treated surface (Figure 6.7A). Chemical robustness of the material was tested by incubating the coated glass in aqua regia for 10 min. Interestingly, the wettability of the coating remained unaltered and the surface functioned properly (Figure 6.7A). Optical transparency of all the treated surfaces was also found to remain unchanged from that of the control (Figure 6.7B). Inset of the figure pictorially represent the treated surfaces. These seem to be highly advantageous for places where frost formation on windshields is a serious concern.

To be used as a non-wettable coating material for day to day use, mechanical stability is a mandatory compliance. This was assessed by knife scratch, peeling off and abrasion tests. These tests were done using scissor, scotch tape and a sand paper (keeping a load of 50 g on the sand paper) (Figure 6.8A, 1-3). For all the cases, even after 20 complete cycles, the coatings remained pristine with uncompromised wetting behavior toward different liquids (Figure 6.8B). Transparency of the treated surfaces also remained intact although there was some sign of knife scratches on the particular surface (Figure 6.8C). Reusability, as well as stability of the coating were further evaluated by write and erase tests (Figure 6.8A,4) where pencil streaks were easily erasable without damaging the unique properties of the coating. In this case also treated surface was also checked for wettability and transparency Figure 6.8B&C). Longstanding durability of the coating to different cyclic perturbations was studied by subjecting the sample to consecutive cycles of different sets of conditions such as high temperature, frost, chemical treatment (organic solvents, oil and emulsion) and exposure to sunlight. Change in the wettability was measured (CA and CAH) after each and every cycle of different sets (details in Chapter 3) which shows a constant value of 134°±2° and 86°±2° for CA and 10°±2° and 4°±2° for CAH on an average for water and toluene, respectively. These values remained unaltered even after 4 different sets of experiments (total of 20 cycles) (Figure 6.8D).

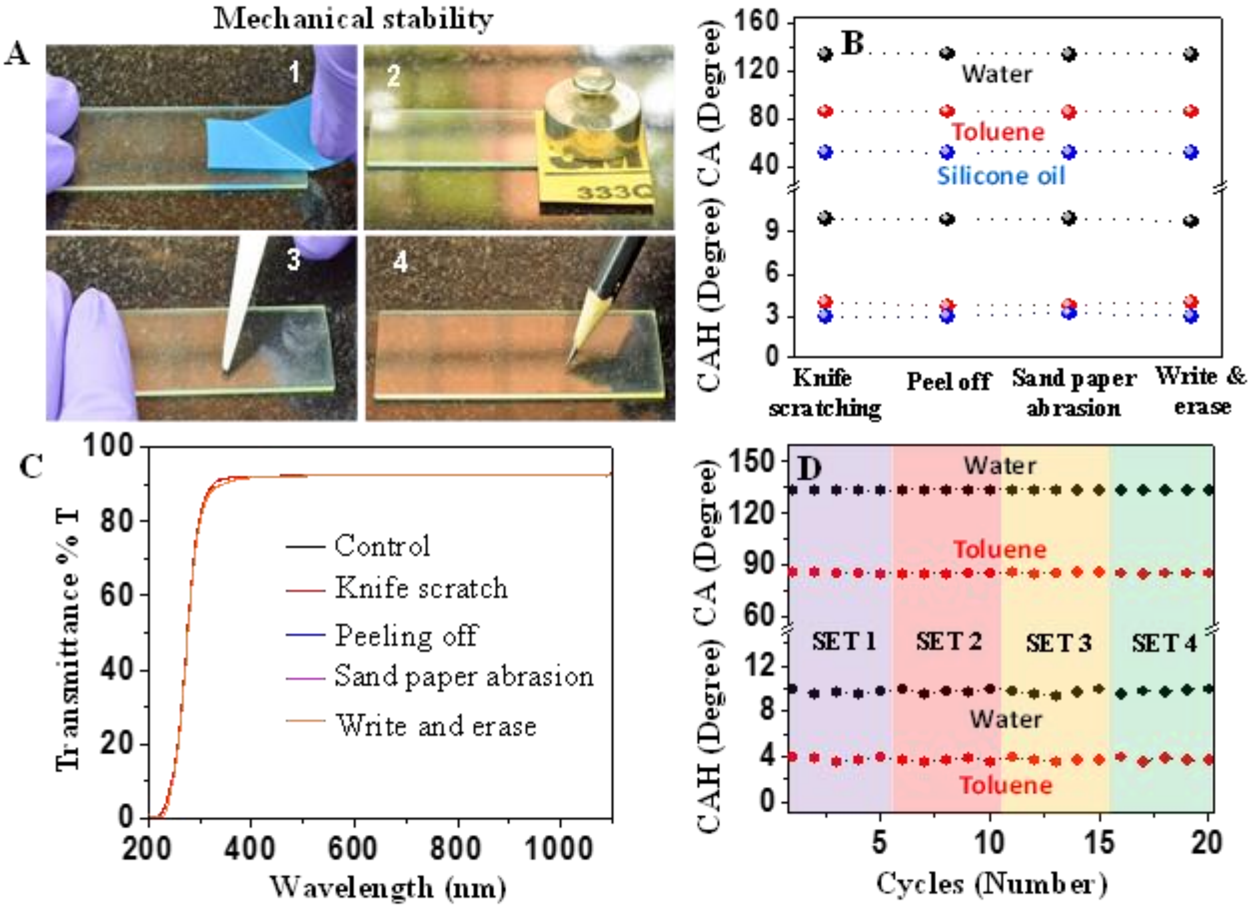


Figure 6.8 (A). Test for mechanical robustness. 1) Peeling off experiment, 2) sand paper abrasion, 3) knife scratch and 4) reusability measurements using write and erase experiments. (B) Wettabiliy of the coated glass surfaces after different mechanical tests (20 cycles). (C) Transparency of the coated glass after mechanical perturbations (20 cycles). The graph shows 99.6 % transmittance of the treated substrates with respect to the untreated control. (D) Durability test in cyclic fashion. Set-1&2. Treating at high temperature (200 ºC) and low temperature (-80 ºC), Set-3. Effect of chemicals (surface was dipped inside different organic solvents, oil and emulsion). Set-4. Direct exposure to sunlight. Reprinted with permission from publication III, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

Application of such materials is not confined to glass substrates alone. To explore the universality or compatibility of the material with different substrates, this material was applied to a wide variety of substrates starting from metal to wood and plastic (Figure 6.9). Consistency in the physical appearance of the original substrates even after the coating provides an added advantage (Figure 6.10). All the substrates (coated glass and wood surface shown here) showed excellent resistance to wetting by nonpolar fluids like oil and oil-water emulsion (Figure 6.11).

Figure 6.9 Universality of the coating. The coatings can be universally applied to all substrates from wood to plastic and the appearance of the substrate remains unchanged even after the coating. Reprinted with permission from publication III, (Baidya *et al.*, 2018) © 2018 John Wiley and Sons.

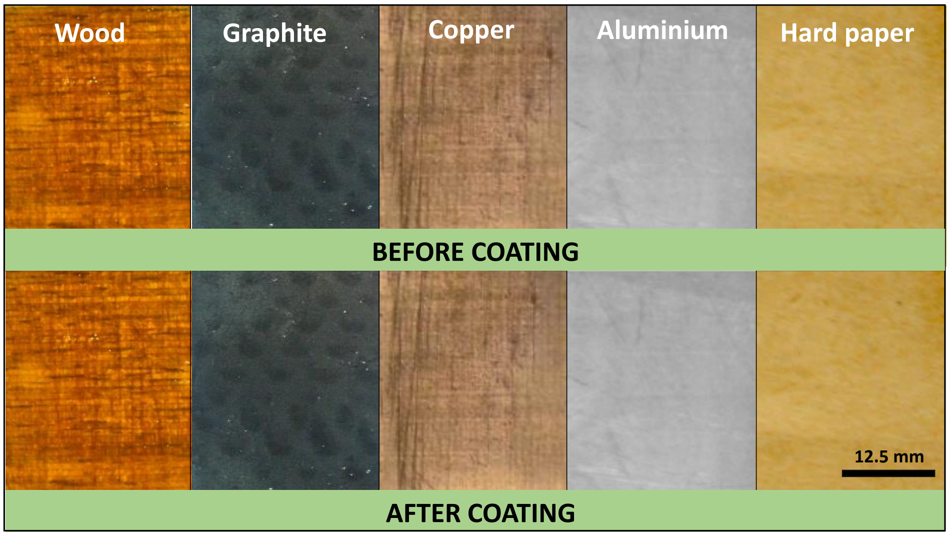


Figure 6.10 Physical appearance of different substrates before and after coating. There was no change in color in wood as there was no temperature fluctuation (see S8, where there was a color change). Reprinted with permission from publication III, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

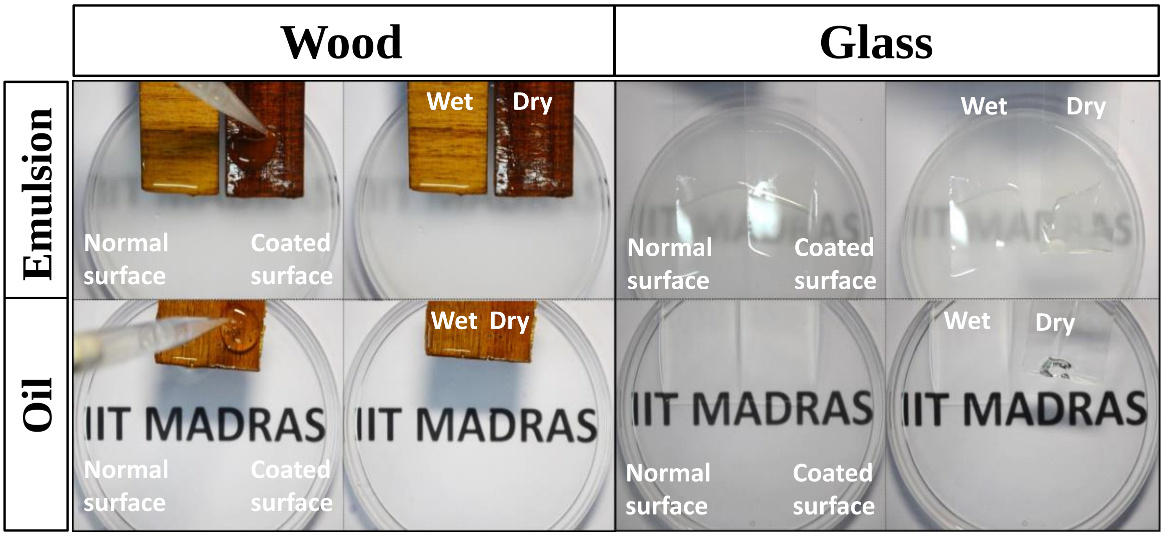


Figure 6.11 Oil (viscous oil and emulsion) repellent slippery nature of the coating (on wood and glass). Change in color and contrast of the wood is because of temperature fluctuations during the sample preparation. See Figure 5.10 for a surface without change in color after coating. Reprinted with permission from publication III, (Baidya *et al*., 2018) © 2018 John Wiley and Sons.

Stability of the coatings on metal substrates was evaluated by treating them with the corrosive acid, aqua regia. The metal surface coated with the newly synthesized material remained unaffected (Figure 6.12A-C) while uncoated surface changed its color immediately with the evolution of hydrogen gas. Figure 6.12D schematically demonstrates effective application of such slippery coatings in real life. Affordable drinking water being a global issue to concern, atmospheric water capture has become a hot topic of research. This needs efficient condensation of humidity and transportation of the droplet formed on the surface. In this context, low hysteresis and low contact angle (high contact area) surfaces having excellent durability can be a good solution as water condenses over such surfaces easily. Figure 6.12E demonstrates a proof of concept experiment. Humidity and temperature are the governing parameters for this phenomenon. At 63% humidity and 27 ºC, our coated surface enables condensation of 5 L of water per m2 in a day. Here, a peltier cooling system was used to cool the surface down to 8 ºC. We believe that the efficiency of such water collection can be maximized by patterning the surface. We note that overall collection efficiency is not only an issue of efficient condensation but also transport which is mostly controlled by the wettability of the surface as well as CAH.

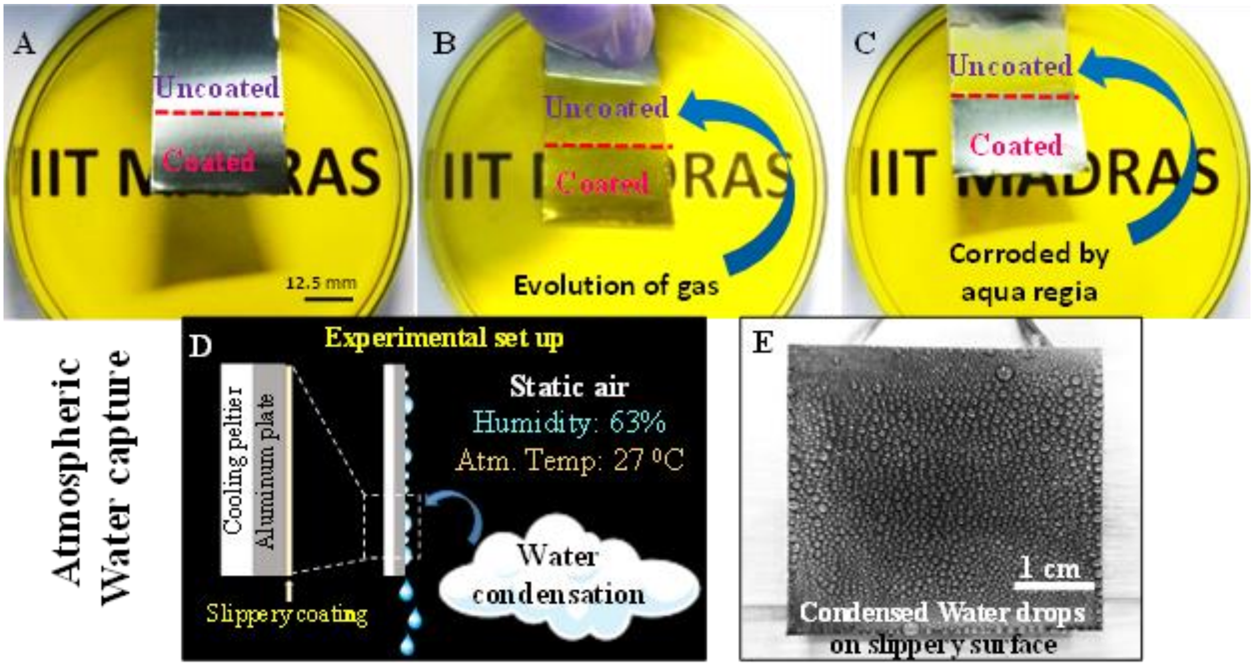


Figure 6.12 Properties of the coated surface. A). Response of the surface to aqua regia treatment. The metal surface (stainless steel) was dipped into aqua regia. B). There was an evolution of hydrogen gas from the uncoated part and (C) it eventually corroded, while the coated region remained intact. D) Schematic representation of atmospheric water capture. E) Real time experimental set up with condensed water drops over the coated surface where surface temperature was cooled down to 8 ºC by a peltier cooling system. The environmental temperature was 27 ºC with 63% relative humidity. Reprinted with permission from publication III, (Baidya *et al.*, 2018) © 2018 John Wiley and Sons.

High liquid repellent nature of the coating originates from the presence of low surface energy molecules as well as the nanostructures formed in-situ. While efficient adhesion property of silanes on the surface of various substrates makes this coating universal, the formation of amorphous silicate structure upon curing, which is inert towards a range of chemicals including strong acids, makes this material robust towards various mechanical and chemical perturbations. Stability and high transparency of the coating at varying temperatures also can be explained easily from the physical and the chemical structure of the material, which are similar to silicate glass.

6.4 Summary

In conclusion, a waterborne, easy to synthesize, robust coating material has been formulated that shows high liquid repellency, without the use of any lubricating fluids. The coating showed excellent stability towards mechanical strains with uncompromised optical transparency. Transparency, as well as liquid-repellent properties of the coating were maintained even after extreme thermochemical treatments. Being a water based liquid material, it enables the creation of large surface area slippery surfaces with a simple coating procedure and decreases environmental concerns and risk of organic solvents at the same time. While extreme repellency towards a wide variety of liquids can widen its industrial use by minimizing transportation cost of fluids through pipelines, transparency in extreme conditions along with other properties can provide easy solutions for display and automobile industries. Beside these, application of this surface towards solving one of the biggest global issues, namely affordable clean/drinking water, is demonstrated as a proof of concept.

CHAPTER 7

Summary and Future Directions

7.1 Summary

Biologically available surfaces that possess different unique liquid repelling properties have attracted scientific communities in many ways and the subject area of non-wettability has become one of the most intensely pursed topics in the past few years. Surface roughness (nano/microscale) and controlled chemical functionalities being the underlying reason for such phenomena, artificially fabricated such surfaces have already proven their huge application potential in different fields of science and technologies that can solve many of our global issues of today and tomorrow. However, most of the time complex multi-step processes, affordability of the initial materials, large scale production and durability (mechanical and chemical) restrict the use of these surfaces in day-to-day life. On the other hand, in the context of coating with chemically modified materials, use of organic solvents, impart concerns related to safety, environmental pollution, operational cost, storage, transport, and many others. In addition, stability or longevity of these surfaces are still questionable, as small mechanical perturbations like gentle touch with tissue paper or finger wiping can damage these surfaces permanently. From an industrial point of view, these have limited the commercialization of these materials as well as in their bulk production.

In view of the current scenario, the work presented in this thesis has focused on the development of coating materials through a green and industrially adaptable or feasible ways that provide durable liquid repelling films over a diverse array of large areas substrates. Water being economical and environmentally accepted solvent system for any kind of bulk production, in the present study, fabrication of these materials was solely carried out in water at room temperature. In the context of primary ingredients, use of affordable and cheap materials like clay and cellulose, enhance the possibility of scaling up and further industrialization of developed methodologies and materials.

In publication I, a simple strategy to develop a durable waterproof paper from cellulose nanofibers building blocks was demonstrated. Wettability of native hydrophilic CNFs was controlled through chemical modification where covalent linkage with low surface energy molecules was carried out solely in water. However, being synthesized and dispersed in water, this material also facilitates its applicability as an environmentally friendly coating material for creating large area superhydrophobic surfaces. This material shows a durable water-resistant property which can withstand multicycle abrasion as well as chemical damages. Finally, chemical functionalization-induced enhancement of integrity (between the fibers) and excellent microbial resistance of the waterproof paper provide a basis for its applications in different paper-based technologies.

Clay being one of the important preliminary ingredients for various commercialized products, in publication II, we have shown a simple, one-step synthesis of clay-based composite material that provides a durable superhydrophobic coating over a wide variety of substrates (without using any adhesive). The material forms superhydrophobic thin films easily at room temperature that withstood various mechanical and chemical stresses. In this case also, the surface showed excellent water repelling property even after various mechanical abrasions such as sand paper abrasion, finger wiping, *etc.* Interestingly, the coated thin film functions equally well at both air-solid and oil-solid interfaces which is due to the controlled surface energy obtained by the incorporated chemical functionalities and hydrophobic effect-induced enhanced surface roughness during the slow evaporation of water from the coating material. Moreover, surface tension-induced better and effective binding capability of the clay sheets with soft and fibrous substrates makes it possible to design a flexible waterproof paper.

Thinking about the huge application potential of transparent coatings, in publication III, we have developed a robust coating material that shows excellent slippery characteristics (towards various liquids, oils, and emulsion) without any lubricating fluids. The coating showed excellent stability towards mechanical strains with uncompromised optical transparency. Transparency, as well as liquid-repellent properties of the coating were maintained even after extreme thermochemical treatments. This widens its possible industrial use in various domains. Beside these, application of this surface towards solving one of the biggest global issues, namely affordable clean/drinking water, is demonstrated as a proof of concept.

7.2 Future Directions

Development of various low surface energy surfaces has vastly expanded in past few years because of their unique applications in different field of science and engineering. These have encouraged researchers to design affordable and rugged surfaces for real-life usages. Although various new materials have been developed, still there is room to fabricate liquid repelling materials with green and eco-friendly materials that can be scaled up easily. Meanwhile, use of various fluorinated molecules also increased the environmental concerns. Therefore, it is important to design materials having excellent liquid repelling properties with chemically safe and affordable molecules.

Most of the cases, these materials are made in laboratory scale and developed protocols only works for small scale production. Therefore, there is a need to research on developing protocols for industrial scale production. Commercial availability of these materials, certainly will help both academia and industries to expand their research field on new applications related to these low surface energy materials.

Although these liquid repelling surfaces have given effective solutions for various global crisis including global water scarcity, I believe, these materials have enormous hidden potential to serve in the context of other important issues related to energy management, air pollution, medical science, solar energy, fuel cell and many others. As most of the time, incorporation of functional materials are seen to impart new dimensions to the materials (according to the incorporated materials) without affecting their inherent properties such as self-cleaning, antifouling, drag reduction and so on, newly designed materials are expected to expand their usage in various purposes.

Finally, the chemistry of these surfaces need to be understood more precisely. It is well-known that the roughness and chemical parameters control the liquid repelling properties of these surfaces. However, how these chemical functionalities are related to the low/ultra-low surface energy of these surfaces are not fully understood and should be studied with theoretical modeling. Moreover, the evolution of such bulk macroscopic property from molecular contributions should be studied in detail. This will assist the development of new kind of multifunctional surfaces for different purposes.

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