A Short Review on Challenges in Fabrication of Oil Repellent Surfaces

[1]Ajay Mittal, [2]Siddharth Verma, [3]S.M.Iqbal, [4]Rajeev Gupta, [5]Manjeet Singh Goyat, [6]Kamalpreet Kaur, [7]Satya Krishna Nippani

[1]Industry Fellow, [2]B.Tech. Student, [3]B.Tech. Student, [4] Associate Professor, [5]Assistant Professor, [6]Assistant Professor,

[7]Assistant Professor
[1]Department of Chemical Engineering, School of Engineering Studies,
[1]University of Petroleum & Energy Studies, Dehradun-248007, Uttarakhand, India

Abstract: During the last few years, emerging research on materials has focused on the fabrication of novel oil repellent surfaces that constitute an essential foundation stone of modern technology in oil industry. In order to fabricate such surfaces, many methods has adopted. Surface energy and surfaces roughness are the critical parameters for fabrication of such surfaces. In this paper, we have reviewed different techniques to modify the surfaces roughness by application of nanoparticles in different materials.

IndexTerms **- oil repellent, nanoparticles, surface roughness**

I. INTRODUCTION

Wettability has been a matter of great significance in the recent past due to its industrial and academic viability {1-5}. Mimicry of nature is a promising way to explain the potential applications of wettability. Many insects and plants have repelled water and sometimes oil from their surfaces. The most common example is of lotus leaf, a drop of water bounces off from the surface of leaf by adsorbing the dirt from its surface by the action of photons and hence showing its hydrophobicity. Along with lotus several other examples which include legs of water striders{6} and troughs of desert beetles{7} have shown significant hydrophobicity i.e. contact angle greater than 150^o with water. Contrary to it, oil significantly wet the surface of lotus leaf, thereby promoting its oleophilic nature. Therefore, superoleophobic surfaces i.e. showing a contact angle greater than 150^o with oil are very rare. Surface tension of organic compounds is way lower then water and hence they are able to wet the surfaces, which are hydrophobic in nature. Here surface tension referred as the magnitude of cohesiveness amongst the drop of wetting substance. Cohesive interactions between the particles of the organic compounds are significantly low. Type of bond formed i.e. surface energies can significantly define the reason behind this lower cohesive interaction. Organic compounds are generally classified in low surface energy group i.e. 10-50 mN/m. They thought to be formed by weak intermolecular force of attraction, thus their cohesiveness is on the lower side. Previous researches and calculations suggest that surface with even less surface energy to repel the oil is yet been uncertain.

Roughness is a complementary part, which is handy in the observations of wettability. Generally, Wenzel and Cassie-Baxter models are used for studying the role of roughness on such surfaces. As per Wenzel {8}:

$$\boxed{\cos \Theta = \boldsymbol{r} \cos \boldsymbol{\alpha}}$$

Where, r is the roughness of surface, ϴ is the apparent contact angle on rough surface, α is the equilibrium contact angle on smooth surface.

As per Wenzel, surface roughness increases the available area for the particles thereby enhancing the wetting when the equilibrium contact angle is less than 90^o. Cassie-Baxter model or generally the Cassie model works on the principle that air particles are trapped between the droplets of sample and the coated surface, thereby, creating a possibility of holding up the droplet due to the pressure from beneath and providing us with a phobic characteristic surface. As per Cassie {9}:

$$\boxed{\cos \Theta = -1 + \emptyset(1 + \cos \boldsymbol{\alpha})}$$

Where, ∅ is the fraction of solid in contact with the liquid, ϴ is the apparent contact angle on rough surface, α is the equilibrium contact angle with the smooth surface. Mathematically, this equation provides us with the possibility of obtaining an apparent contact angle greater than 90 degree even with an equilibrium contact angle of less than 90^o.

These two models have described the importance of air, which is trapped in between the solid and the liquid. By taking this conclusion, Tuteja et al {10} has introduces a new factor in the creation of Superoleophobic coatings. Re-entrant surfaces like micro Hoodoos, mat like electro spun structures and pillar like structures are developed. They enhances the possibility of air entrapment and hence oleophobicity. Photolithography and etching are used for the creation of re-entrant structures. Photolithography includes the usage of UV rays to generate micro fabrications on the surface of substrate by using a photo resist and then with the help of etching engraving the desired pattern to trap the air.

II. CLASSIFICATION OF MATERIAL:

2.1 INORGANIC MATERIAL

This group consists of mixture of PDMS and Zinc Oxide (ZnO), mixture of TX_xCL_5Si/TEOS or $GalCL_5Si$/TEOS dissolved in THF, fluoropolymer and DMF $DDSiO_2$ solution, fluorodecyl POSS, silica nanoparticles under the influence of perfluoroalkylmethacrylic copolymer etc. All incorporated materials mentioned above produce coating which satisfy the conditions of oleophobic coating i.e. low surface energy, surface roughness and generation of concave structures on the surface along with an excellent unsticking ability for droplets which is what makes the self-cleaning. To avoid damage to the coating in some cases secondary coating is done like in DMF DDSiO_2 additional fluoropolymer coating is done to increase the adhesive forces between the molecules.

2.2 ORGANIC MATERIAL

Many plants and animals display excellent oleophobicity through years of evolution for increasing their survivability for example Springtails, Fish scales, clam's shell, seaweed etc. While lotus leaf is known to have hydrophobic nature experimental data's show that it's back side is able to exhibit There are other derived materials like alginate which is a polysaccharide from brown marine algae which are low cost and easily available and when this alginate crosslinks with Ca^{+2} to form calcium alginate which exhibits oleophobicity in nature.

III. SUBSTRATES USED FOR THE FABRICATION OF SUPER OLEOPHOBIC COATINGS:

Surface energy of the substrate is the determining factor for developing any kind of coatings. It is clear that no known material is having sufficiently low surface energy that it can be used to serve the purpose. In the scientific terminologies, we have focused a lot upon rigid surfaces for research purposes.

3.1 RIGID SUBSTRATES

Each experiment of Tuteja et al {10-11} have focused upon silicon wafers as a substrate, altering surface topography to produce micro-hoodoos structure is the reason. Moreover, the industrial applications of super oleo phobic coatings may not require transparency at its best. However, it is environmentally hazardous because of the fluorinated compounds being used but the most effective till date. It is believed that super oleo phobic coatings can also be developed upon the glass or steel substrates (Li-Ping Xu et al) {12}. Solid rigid substrates are not usually preferred to develop coatings because rigidity will limit the use of coating in industrial applications. Surface roughness and surface chemistry is an important factor, which usually defines a substrate. The mineralogical composition of any substrate will define its surface energy and thereby its use.

3.2 FLEXIBLE SUBSTRATES

Many organic and inorganic compounds along with polymers are giving us a possibility to develop flexible substrates by using cellulose as a substrate. Li-Ping Xu et al {12} have proposed the use of Alginate which is a naturally occurring poly anionic polysaccharide produced by brown algae, it is environmentally safe. They have used various substrates including Polyethylene teraphthalate (PET) and mica. Atsushi et al {13} have used organosilanes specific length chains to generate oleo phobic coatings and various other polymers, which include few conventional polymers, were also used. Flexible substrates can be used in various industrial applications, which may include bending the substrate and much more. Therefore, we can conclude that flexible substrates have more robustness and practical implications. It is believed that fibrous texture can significantly impart oleo phobic characteristics and therefore can be used as substrates.

IV. APPROACHES FOR FABRICATION OF SUPER OLEO PHOBIC SURFACES:

Coatings are generally fabricated over substrates by three methods: top down method, bottoms up method and combination of both. Among the three, the most commonly used method is top down approaches, which generally uses surface alteration techniques like lithography, etching and few more. However, while developing super oleo phobic coatings a combination of both is usually used. The re-entrant structures are developed on the surface of substrate to act as an air pocket and thus compensating for the low surface energies. (Tuteja et al). Combination of both involves the use of many other techniques as well, which include electro spinning and phase separation.

4.1 TOP DOWN APPROACHES

The most commonly used method is the top down approach. Top down is a broad term, which is used in many aspects. Top down is majorly used for mentioning the manufacturing of materials, treatment of surfaces and devices to get the desired results (R.K.Gupta et al){14}. Surface alteration is majorly considered in top down approach. Surface topology is altered in such a manner so as to develop air pockets on the surface. Air pockets will trap the air and balance the droplets of oil above the surface so as to make it an oleo phobic surface. It includes many techniques like:

4.1.1 LITHOGRAPHY, TEMPLATE BASED & ETCHING

Fabricating structures over the surface can be done easily by using lithography. On broader terms photo lithography, electro lithography, X-ray lithography are used to generate nano structures on the topology of substrate surface. Fig.1 depicts the methods adopted by different researchers to develop the hydrophobic coating on the different materials.

Hak-Jong Choi et al{15} have developed overhang structures on substrate by using nanoimprint lithography to ultimately develop oleo phobic coatings. Different patterns of nano structures are observed by them to alter the angles of overhang and thereby enhancing the oil repellency.

Dawai Zhang et al{16} altered the surface topography of PDMS template using sandpaper which is further used to alter the topography of epoxy coating on steel substrates and thereby imparting extra hydro phobicity to the surface.

Juan Li et al {17} worked upon the self-transportation of oil droplets by using lithography obtained patterns. They developed radial micro strips patterns on the surface coated with TiO_2 to enhance the oil repellency. They had used photolithography followed by ionic etching to achieve this undercut pattern on silicon wafer substrate. The radial pattern is preferred as it readily accumulates the oil in the middle by self-transportation.

Photolithography followed by dual etching is used by tuteja et al to develop oleo phobic as well as omniphobhiccoatings on silicon wafer. They created micro hoodoos structure along with electro spun fiber mat like structure, which can both trap air to easily repel oil. They have succeeded in doing so by primarily etching silicon wafer by reactive etching of SiO_2 followed by isotropic etching of Si with the use of vapor phase XeF_2. Following the process, they obtained a static contact angle of 143^o, which is super oleo phobic. Most of the groups working on the oil repellency are looking on photolithography with great hopes when compared with other methods of lithography. This is because of its versatility to be used with UV, X-ray and electric beams etc. Added to it, photolithography along with ionic etching is a very fast pace method when compared with other methods.

Arun Kumar Gnanappa et al {19} used Oxygen plasma etching & colloidal lithography for alteration in morphology of PMMA plexiglass plates. They observed that Plasma induced nano texture followed by Fluorocarbon plasma deposition of 40 nm grows linearly with time, lithography followed by etching imparted fibrous morphology to substrate forming tree like nano fibres.The developed morphology was mechanically robust and was super hydrophobic with a static contact angle of 155 degrees and at the same time by varying the intensity of etching showed super oleo phobicity by imparting a static contact angle more than 150 degrees. It was observed that with an increase in etching time the contact angles increases. With increase in relaxation time, surface contact angle for oleo phobic coatings develop instead of dropping which signifies its robustness.

K.Ellinas et al{20} demonstrated nearly similar experiment to Gnanappa et al but the results observed by them were slightly better as the static contact angle for water in their case was 168 degrees, whereas for diiodomethane static contact angle was 153 degrees. They focused more upon spacing, heating, nona texturing, re-entrant profile by which wettability will be controlled more effectively. They tried to demonstrate the importance of bias voltage and etching time, height and diameter of nano textured pillars depend upon them. Ellinas et al focused upon the development of super hydrophobic and super oleophobic surfaces of polymer such as PDDA, PDMS etc. by using ion enhanced plasma etching whose intensity will vary in accordance with the polymer in use followed by deposition of perfluoroodecyltrichlorosilanemonolayes, which will alter the surface energy of the substrate thereby supplementing repellency. By doing so they generated nano textured layers which in turn will give us static contact angles in super phobic ranges. For water and oil the static contact angle was greater than 153 degrees.

Seong Min Kang et al {21} focused upon developing mushroom like nano pillars on the substrates of PDMS and PDFE. They influence much upon the mushroom structure of nano pillars because they can provide both mechanical robustness and energetically favorable omniophobic surfaces. Overhang structures can also provide the desired results but they will not remain in cassie-baxter state for long time and thus will not be durable. They evaluated the super omniophobic characteristics by using water and ethanol. They observed their static contact angles and contact angle hysteresis for serving both the purposes. Spacing ratios must be greater than 4 so as to get an oleo phobic texture. Fluorocarbon surface treatment was given to supplement the omniophobicity by decreasing the surface energy further.

Rajendra Kumar et al {18} formed nano grass on silicon wafer by using inductive coupled reactive etching process. Etching process can be considered as a substitute of lithography when we have to randomize the things. The operating conditions were: deposition time was taken as 5 minutes, coil power as 2800 watt, pressure was taken as 28 mTorr, temperature was considered constant at 10 degree centigrade. SF_6 and O_2 flow rate was varied to alter the angle of nano grass which will directly affect the static contact angle (115-151 degrees), after this fluoro compound deposition takes place.

Lee et al {22} focused upon creating re-entrant surfaces by using molding and etching. They developed superamphiphobic surfaces on flexible substrates where the droplet bouncing and higher transparency were achieved. The Polyurethane Acrylate mold was coated with PMMA; the mold was then brings in contact with the substrates at specified temperature and pressure conditions for two minutes to transfer molding. The excess of PMMA was removed by using O_2 etching followed by final etching to give undercut shape. The observed result includes: Contact Angle 151 degrees for Ethylene Glycol, Ethanol (146) and Toluene (141). Thus, it behaved as both super hydrophobic and super oleo phobic.

Nguyen et al {23} focused on the development of super omniphobic surfaces by single and double re-entrant surface formation. It was observed that best possible value of Static Contact Angle for both water and organic samples appears for dual scale texturation i.e. a combination of micro pillars and nano wires. Silicon polished on one side is used as substrate which is rinsed properly with acetone and cleaned in piranha solution then AZnLOF 2035 is spin coated over the substrate at 3000 rpm. Then, the silicon wafer was etched using deep reactive ion. Fabrication of double scale was developed to get good oil and water repellency.

So by the above discussion we can conclude that lithography is the best method to produce desired surface topographies at substrates by using photo resist and master surfaces. Template based uses a master piece over which our desired 2-D or 3-D pattern is embossed and will be replicated on numerous other surfaces to alter the surface topography. Etching must be regarded as the best method for producing roughness and randomness on the topography of substrate.

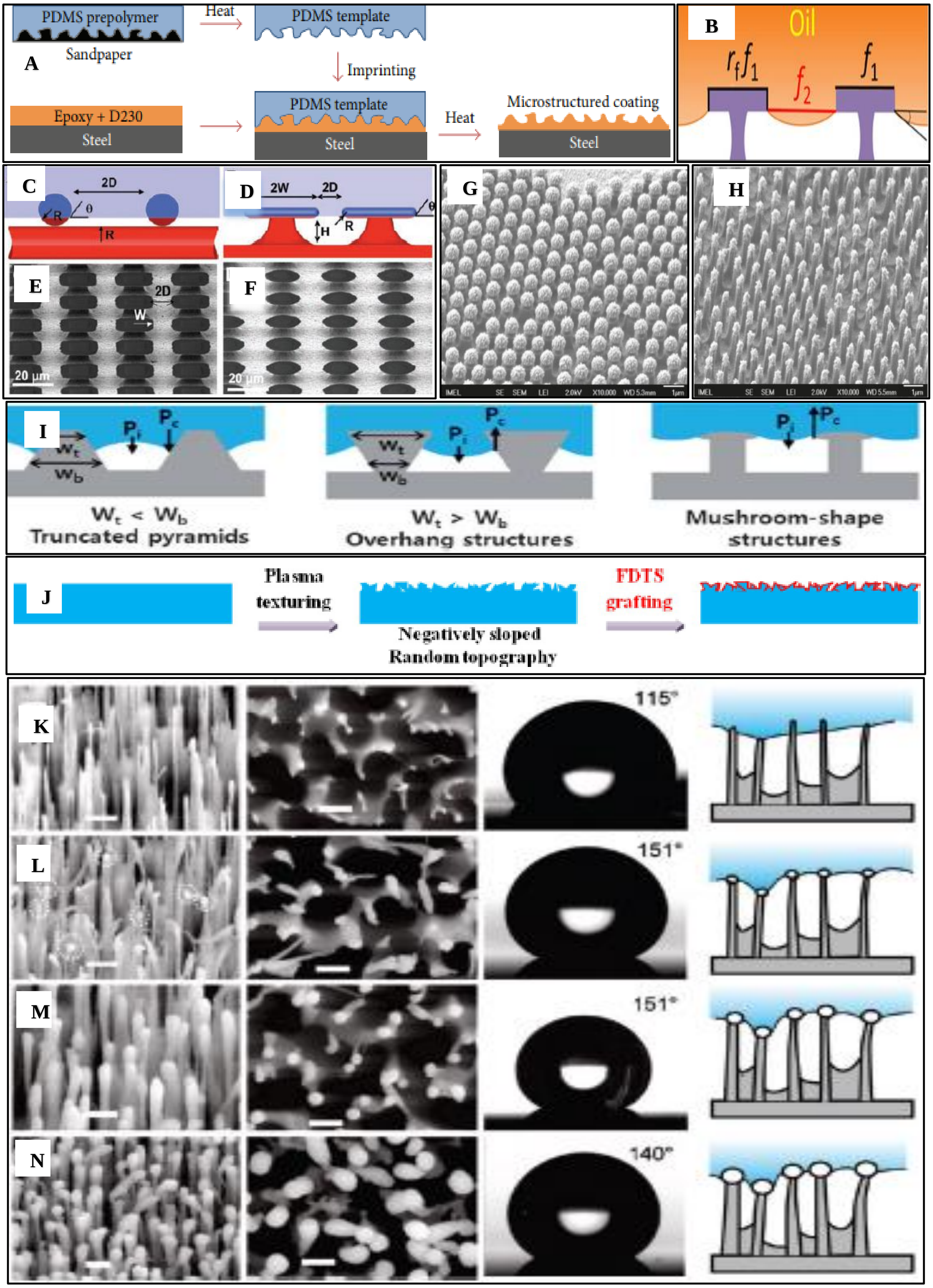

Fig 1: Methods adopted by researchers for enhancing hydro phobicity: (A) - Etching Method by Dawai Zhang et al, (B) - Lithography Method by Juan Li et al, (C, D, E, and F) - Combination of Lithography and Etching by Tuteja et al, (G and H) - Combination of Lithography and Etching by K. Ellinas et al, (I) - Lowering Surface Energy by Seong Min Kang et al, (J) - Etching Method by Ellinas et al, (K, L, M and N) - Etching Method by Rajendra Kumar et al.

V. CONCLUSIONS

This paper reviewed the top down approaches for fabrication of oil repellent surfaces by creating Micro/Nano order roughness, which have wide spread application to reduce the wax deposition in oil pipelines during transportation of crude oil, corrosion control, oil–water separation, microfluidics, anti-graffiti, biomedical membranes and devices, etc. This study will help the researchers in understanding existing technologies in developing new oil repellent surfaces with improved stability and mechanical characteristics.

REFERENCES:

1) Dorrer, C., & Rühe, J. (2008). Wetting of silicon nanograss: From superhydrophilic to superhydrophobic surfaces. Advanced Materials, 20(1), 159–163. https://doi.org/10.1002/adma.200701140
2) Feng, X., & Jiang, L. (2006). Design and creation of superwetting/antiwetting surfaces. Advanced Materials, 18(23), 3063–3078. https://doi.org/10.1002/adma.200501961
3) Quéré, D. (2005). Non-sticking drops. Reports on Progress in Physics, 68(11), 2495–2532. https://doi.org/10.1088/0034-4885/68/11/R01
4) Verplanck, N., Coffinier, Y., Thomy, V., & Boukherroub, R. (2007). Wettability switching techniques on superhydrophobic surfaces. Nanoscale Research Letters, 2(12), 577–596. https://doi.org/10.1007/s11671-007-9102-4
5) Esmeryan, K. D., McHale, G., Trabi, C. L., Geraldi, N. R., & Newton, M. I. (2013). Manipulated wettability of a superhydrophobic quartz crystal microbalance through electrowetting. Journal of Physics D: Applied Physics, 46(34). https://doi.org/10.1088/0022-3727/46/34/345307
6) Gao, X., & Jiang, L. (2004). Water-repellent legs of water striders. Nature, 432(7013), 36. https://doi.org/10.1038/432036a
7) Parker, A. R., & Lawrence, C. R. (2001). Water capture by a desert beetle. Nature, 414(6859), 33–34. https://doi.org/10.1038/35102108
8) Wenzel, R. N. (1936). Resistance of solid surfaces to wetting by water. Industrial and Engineering Chemistry, 28(8), 988–994. https://doi.org/10.1021/ie50320a024
9) Cassie, A. B. D., & Baxter, S. (1944). Of porous surfaces,.Trans. Faraday Soc., 40(5), 546–551. https://doi.org/10.1039/TF9444000546
10) Tuteja, A., Choi, W., Ma, M., Mabry, J. M., Mazzella, S. A., Rutledge, G. C., Cohen, R. E. (2007). Designing superoleophobic surfaces. Science, 318(5856), 1618–1622. https://doi.org/10.1126/science.1148326
11) Tuteja, A., Choi, W., Mabry, J. M., McKinley, G. H., & Cohen, R. E. (2008). Robust omniphobic surfaces. Proceedings of the National Academy of Sciences, 105(47), 18200–18205. https://doi.org/10.1073/pnas.0804872105
12) L. P. Xu, D. Han, X. Wu, Q. Zhang, X. Zhang, and S. Wang, “A green route for substrate-independent oil-repellent coatings,” Sci. Rep., vol. 6, no. November, pp. 1–6, 2016.
13) Hozumi, A. & Urata, C. Development of environmentally-friendly surface modification technology. Synthesiology 7, 190–198 (2014).
14) Gupta, R.K.; Kumar, P.; Yadav, V.; Arora, S.; Singh, D. P.; Joshi, S. K.; Chawla, A. K. Challenges and Opportunities in Fabrication of Transparent Super- Hydrophobic Surfaces. 2016, 429–447.
15) Choi, H.; Choo, S.; Shin, J.; Kim, K.; Lee, H. Fabrication of Superhydrophobic and Oleophobic Surfaces with Overhang Structure by Reverse Nanoimprint Lithography. 2013, 24359 (2).
16) Zhang, D., Li, H., Chen, X., Qian, H. & Li, X. Effect of surface microstructures on hydrophobicity and barrier property of anticorrosive coatings prepared by soft lithography. Adv. Mater. Sci. Eng. 2014, (2014).
17) Li, J.; Qin, Q. H.; Shah, A.; Ras, R. H. A.; Tian, X.; Jokinen, V. Oil Droplet Self-Transportation on Oleophobic Surfaces. 2016, No. June, 1–7.
18) Thangavelu, R.; Kumar, R.; Mogensen, K. B.; Bøggild, P. Simple Approach to Superamphiphobic Overhanging Silicon Nanostructures. 2010, 7, 2936–2940.
19) Gnanappa, A. K. et al. Hierarchical, plasma nanotextured, robust superamphiphobic polymeric surfaces structurally stabilized through a wetting-drying cycle. Plasma Process. Polym. 9, 304–315 (2012).
20) Ellinas, K.; Tserepi, A.; Gogolides, E. From Superamphiphobic to Amphiphilic Polymeric Surfaces with Ordered Hierarchical Roughness Fabricated with Colloidal Lithography and Plasma Nanotexturing. 2011, 3960–3969.
21) Kim, S. M.; Kang, S. M.; Lee, C.; Jang, S.; Kim, J.; Seo, H.; Bae, W.; Yang, S.; Yoon, H. By Mechanical Pulling †. J. Mater. Chem. C 2016.
22) Lee, S. E., Kim, H. J., Lee, S. H. & Choi, D. G. Superamphiphobic surface by nanotransfer molding and isotropic etching. Langmuir 29, 8070–8075 (2013).
23) Phuong, T.; Nguyen, N.; Brunet, P.; Coffinier, Y.; Boukherroub, R. Quantitative Testing of Robustness on Superomniphobic Surfaces by Drop Impact. 2010, 1 (14), 18369–18373.