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Techniques for the Fabrication of Super-Hydrophobic Surfaces and Their Heat Transfer Applications

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Abstract

Super-hydrophobic surfaces are surfaces that have extreme water-repellent properties and show contact angle greater than 150° and sliding angle less than 5° . These surfaces play a significant role in different processes like icing delay, anti-frosting, boiling, condensation, drag reduction, self-cleaning, etc. The present study comprises of different techniques for the fabrication of super-hydrophobic surfaces. These techniques include chemical etching, solution immersion, laser electrodeposition, template deposition, spray coating, various others. Important characteristics of super-hydrophobic surfaces like durability, storability, corrosion resistance, etc. are achieved differently by different methods. Also, some methods are simple, rapid, cost-effective and versatile. Moreover, various heat transfer applications of super-hydrophobic surfaces like boiling, condensation, icing delay, drag reduction, etc. have also been discussed in this chapter.

Keywords: super-hydrophobic surfaces, contact angle, sliding angle, surface roughness, micro-nanostructures, surface energy

1. Introduction

It has already been found that leaves of some plants like Lotus flower, Nasturtium, Prickly pear, etc. and wings of some insects like *Pamassius glacialis*, etc. have micro-nanostructures on their surfaces which have ability to repel water excellently [1]. These structures lead to minimum surface energy (i.e. wettability) due to which the contact area fraction between liquid and solid surface also becomes minimum. Moreover, surface tension of liquid causes its droplets to get shaped into spherical shape which has minimal surface area. So, the combined effect of high surface tension of liquid and low surface energy can lead to the formation of spherical

Figure 1. Water droplet in (a) Wenzel state (b) Cassie-Baxter state [2].

drops on the surface. The contact angle of these drops can be more than 150° on such surfaces. Such surfaces are named as super-hydrophobic surfaces. Water droplets can actually bounce on these surfaces. By mimicking the nature, these surfaces can be synthesized.

A liquid droplet can be in two different states when resting on a solid surface which is hydrophobic. In Wenzel state, the liquid droplets penetrate into the asperities of surface resulting in increased contact area fraction of liquid with solid surface. This leads to the reduced mobility of droplets on surface. On the other hand, in Cassie-Baxter state, droplet stays on the hierarchical structures and air gets entrapped in the cavities of surface due to which it has minimum contact area fraction with solid surface. This helps in the formation of spherical droplets which can roll on the surface. Water droplets stay on the super-hydrophobic surface in Cassie-Baxter state [2].

Figure 1 shows the water droplet in Wenzel and Cassie-Baxter state.

First section of this chapter summarizes different techniques for the fabrication of super-hydrophobic surfaces. These surfaces must possess some important characteristics like durability, corrosion resistance, etc. which are required in various applications. The challenge nowadays is the fabrication of super-hydrophobic surfaces which have long-term stability. Second section gives an idea of different heat transfer applications of super-hydrophobic surfaces. Major applications like condensation, boiling, anti-icing and drag reduction with experimental work of different authors have also been discussed.

2. Fabrication techniques

Fabrication of super-hydrophobic surfaces usually requires the roughening of surface to get micro-nanostructures followed by surface modification which leads to low surface energy. Some methods like chemical etching, solution-immersion process, spray coating use coating material for surface modification after surface roughening, while some methods like laser electrodeposition, template deposition do not need to modify the surface. Simplicity, least time consumption, cost-effectiveness and versatility are the important parameters during fabrication process. Moreover, characteristics like durability, corrosion resistance and storability of super-hydrophobic surfaces formed are achieved at different levels from each method.

2.1. Chemical etching

Esmaeilirad et al. [3] developed physically and thermally stable SHS by a simple and cost-saving method. Chemical etching method was used for developing micro-nanostructures on

the surface of Al alloy which was used as a substrate. After surface roughing of substrate with abrasive paper and ultrasonically cleaning with deionized water, it was treated with NaOH first and then with solution of HCl and CH_3COOH resulting in micro-nanostructures on surface. Then surface energy of etched substrate was lowered by immersing it in the solution of silanes. The maximum water contact angle (WCA) obtained was 165° and contact angle hysteresis (CAH) was 3° . SHS formed remained stable after different tests and was storable for more than a month. Qi et al. [4] developed a rapid fabrication method of SHS. Metal-assisted chemical etching was done on zinc plate which was used as substrate. Pure zinc plate was first ultrasonically cleaned and dried in oven. For surface roughing, it was put in an aqueous solution of nitric acid and metal nitrate. Metal nitrates used were AgNO_3 , $\text{Cr}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$. After etching, sample was immersed in a solution of ethanol and fluoroalkyl silane (FAS) for surface modification. WCA of pure zinc without etching was found to be $102 \pm 3^\circ$ after modification by FAS only and maximum of $135 \pm 2^\circ$ with just etching. The maximum WCA was obtained to be $140 \pm 2^\circ$ for $\text{Cr}(\text{NO}_3)_3$ after 5 s, $157 \pm 2^\circ$ for $\text{Cu}(\text{NO}_3)_2$ after 1 s and $162 \pm 2^\circ$ for AgNO_3 after 1 s. In case of Cu^{2+} -assisted chemical etching, etching time, concentration of $\text{Cu}(\text{NO}_3)_2$ and concentration of HNO_3 were optimized.

Figure 2 shows the schematic illustration of Zn SHS fabrication by metal-assisted chemical etching.

Chu and Wu [5] fabricated SHS on Al and Cu substrates simultaneously using chemical etching method. Surfaces were first cleaned and then solution of HCl and $\text{Cu}(\text{NO}_3)_2$ was used for Al plate etching, while for copper plate etching, solution of HNO_3 and AgNO_3 was used. Surface modification was done using aqueous solution of FAS. The results showed that for Al and Cu substrates, the micro-nanostructures were similar to that of lotus leaves and moss, respectively. The WCA was found to be $164 \pm 1^\circ$ for Al and $157 \pm 1^\circ$ for Cu. The measured rolling angles were $2 \pm 1^\circ$ and $6 \pm 1^\circ$ for Al and Cu, respectively. Moreover, condensation experiment was also performed over both SHS resulting in lower droplet density, higher droplet jumping probability, slower droplet growth rate and lower surface coverage for Al as compared to Cu. Yin et al. [6]

Figure 2. Schematic illustration of fabrication of Zn SHS by metal-assisted chemical etching [4].

developed SHS using chemical etching method. Al plate was used as the substrate material. For etching process, a solution of HF and HCl in deionized water was prepared. Later, Al substrate was immersed in that solution for roughing the surface. For surface modification, three different coatings such as perfluoroalkyltriethoxysilane (PFO), PA and room temperature vulcanized (RTV) coating were separately used to determine the super-hydrophobic nature of surfaces. WCA measurements showed the maximum CA of 162, 161.7 and 158.3° for PFO, PA and RTV coatings, respectively. Environmental factors varied, that is, temperature in range of –10 to 30°C and RH values of 30, 60 and 90%, during condensation experiment to determine any changes in super-hydrophobic nature of surfaces. CA, SA and contact area fraction were calculated and it was found that with increasing RH and lowering temperature, CA and SA values decreased and increased, respectively, while contact area fraction increased showing increase in wettability. Super-hydrophobicity of RTV coating was greatly affected during condensation at low temperature which was recovered simply by drying.

To counter the problem of ice accumulation on Al substrate which has excessive use in transmission lines, Liao et al. [7] made SHS on Al which showed excellent anti-icing property. A simple continuous chemical etching method was used for this purpose. The roughness on Al foil was increased by using emery paper and then washed and cleaned properly. For etching process, it was first immersed in CuCl_2 solution and then in HCl solution. Both resulted in increased surface roughness of Al foil. Finally, hexadecyl-trimethoxy silane was used for surface modification which reduced surface energy resulting in super-hydrophobic Al surface. WCA measurements showed that bare Al surface was transformed into SHS with contact angle increasing from 101.1° to 161.9°. It was found after thermal stability tests that WCA reduced a little with increase in temperature but surface was still super-hydrophobic. It was determined that the fabricated SHS could mitigate freezing process. Moreover, stability of SHS was also confirmed against water-drop impact and sand-impact abrasion. Nguyen et al. [8] fabricated super-hydrophobic and oleophobic surfaces using electroless etching method. Silicon surface was used as substrate which was first dipped in $\text{AgNO}_3/\text{NaBF}_4$ solution. This resulted in etching of silicon surface creating nanostructures. This etched surface was then coated by Ag nanoparticles which modified the surface topology. Third and last step was the lowering of surface energy, first by C_4F_8 plasma deposition and second by SiO_x overlayers chemically modified with PFTS. Contact angle of water and hexadecane droplets were measured. When C_4F_8 plasma deposition was used for lowering surface energy, then nano-Si structure showed maximum CA of 160 and 87° for water and hexadecane, respectively. Results were 160 and 110°, respectively, for water and hexadecane when SiO_x overlayers chemically modified with PFTS were used for lowering surface energy. It was found that deposition of Ag particles led to improved wetting properties.

Yin et al. [9] developed a novel way for fabrication of SHS. Al alloy was used as substrate which was properly polished and then washed. It was then anodized under constant current in a particular solution. The next step was chemical etching resulting in leaf-like structure on surface. Last step was the modification of sample with solution of KH-832 in ethanol which decreased the surface energy of sample. Untreated sample was found to be hydrophilic with WCA of 79.4°, sample after pre-treatment and anodization showed super-hydrophilic nature with 0° WCA while sample after pre-treatment, anodization as well as chemical modification was found to be super-hydrophobic with WCA of 167°. SHS formed was also found stable

with contact angle decreasing only 4–7° after 3 months. It also possessed great corrosion protection. Lin et al. [10] used Ti6Al4V as substrate material on which SHS having 3D porous structures, was fabricated. The process of fabrication started with sand blasting of samples resulting in microscale pattern structures. After that, etching was done in two steps. In first step, above samples were immersed in a solution of H₂SO₄ to get microscale pits. Second step of etching was done using alkaline solution and it resulted in porous structures on surface. The samples were then annealed at a temperature of almost 500°C followed by lowering surface energy by modification with FAS-17 solution. NaOH concentration varied during fabrication process and it was found that the best concentration was in range of 2.5–3.5 M. WCA was determined to reach maximum of 160° and SA was 3°. SHS formed by this process also showed very good corrosion protection behavior based on electrochemical corrosion results.

Choi et al. [11] developed a facile and cost-effective approach to fabricate SHS from easily available and environment-friendly materials. Fabrication process was started by pouring polydimethylsiloxane (PDMS) solution on substrate followed by spin coating to make it flat. Then salt particles were introduced on hot embedded PDMS surface. In the last step, dissolution of salts was done by dipping sample into water bath. This resulted in etching of only salt particles and not PDMS that produced micro/nano-hierarchical structures. Surface was modeled as in Cassie-Baxter state with WCA of 151° as compared to 102° for flat PDMS surface without etching. Dust removal experiments showed that SHS formed were capable of self-cleaning. Moreover, SHS had great corrosion resistance properties with droplets of acid/alkali solutions showing contact angles in range of 147–152°.

Table 1 summarizes the work of different researchers who have used chemical etching method for SHS fabrication.

2.2. Solution immersion

Xu et al. [12] developed a simple one-step method of SHS fabrication. Solution-immersion process was used in which copper foams were used as substrate. Pure copper foams after properly washed, ultrasonically cleaned and dried were immersed in ethanolic stearic acid solution for 4 h, 2 days and 4 days. With increase in immersion time, clusters formed became denser, covered the surface more, the skeleton of 3D porous structure got thicker and rougher while pore size decreased. WCA kept increasing with immersion time to 156° for 4 days and SA decreased to minimum of 4°. This fabrication process resulted in robust and mechanically stable SHS. Zhao et al. [13] developed a simple and pure chemical approach of fabricating SHS. SiO₂-coated SiC nanowires were used as substrate material which already contained nanostructures on surface. Fabrication process started with the preparation of ethanol solution of FAS. The substrate was then immersed in the solution for a day which resulted in the surface with super-hydrophobic nature. The treatment process did not produce any change in the surface morphology, micro-texture and crystal phase of substrate. WCA of 5 µL droplet was measured to be 153°. To check for durability, SHS fabricated was irradiated by UV lamps of 100 W which resulted in the great durability of surface. Zheng et al. [14] fabricated SHS on glass substrate by dip coating sol-gel process. At first, glass plate was properly washed and cleaned. Then, two solutions named as 'A' and 'B' were first prepared. Solution 'A' contained glycidoxyparyl trimethoxysilane (GPTS) modified with silica sol while solution 'B' consisted of PTFE emulsion.

Ref. no	Substrate	Materials used	Coating materials for lowering surface energy	Max. water contact angle/ min. sliding angle	Stability	Remarks
[3]	Aluminum alloy	(1) Cast aluminum alloy (2) Hexane (3) (TCODS) (4) (TCDS) (5) (TCOS) (6) Sodium hydroxide (7) Hydrochloric acid (8) Acetic acid (9) Deionized water	Solution of (TCODS + TCDS + TCOS) & hexane	165°/3°	Remained stable after (1) 100 h immersing in water (2) 30 min ultrasonication (3) (3) Heated to 375°C for 20 min	Cost-effective method to create physically stable, thermally stable and storable SHS
[4]	Zinc	(1) Zinc plate (2) FAS (3) Silver nitrate (4) Copper nitrate (5) Chromium nitrate (6) Anhydrous ethanol (7) Nitric acid	Solution of ethanol and FAS	(1) When AgNO ₃ : 162 ± 2° (2) When Cu (NO ₃) ₂ : 157 ± 2° (3) (3) When Cr (NO ₃) ₃ : 140 ± 2°	WCA remained almost constant for 7 months in air	A fast method to fabricate SHS, good for metals
[7]	(1) Aluminum (2) Copper	(1) Aluminum foils (2) Copper foils (3) Fine sand paper (4) Absolute ethyl alcohol (5) Cu(NO ₃) ₂ ·3H ₂ O (6) Pure HCl (7) AgNO ₃ (8) Pure HNO ₃ (9) 1H,1H, 2H, 2H-Perfluorodecyltriethoxysilane (10) Deionized water	1H,1H, 2H, 2H-Perfluorodecyltriethoxysilane	(1) For aluminum: 164° (2) For copper: 157°	–	A simple chemical etching method for fabrication of SHS on Aluminum and copper substrate
[13]	Aluminum	(1) Aluminum plates (2) Methanol (3) Acetone (4) Toluene (5) Xylene (6) HF (7) HCl	(1) PFO coating (2) PA coating (3) RTV coating	(1) When PFO coated: 162.0 ± 2.2°/0.4 ± 0.1° (2) When PA coated: 161.7 ± 1.9°/2.5 ± 1.0° (3) When RTV		Effect of environmental factors on super-hydrophobic behavior of surfaces was also studied

Ref. no	Substrate	Materials used	Coating materials for lowering surface energy	Max. water contact angle/ min. sliding angle	Stability	Remarks
		(8) Perfluoroalkyltriethoxysilanes (9) Palmitic acid (10) Silicon rubber (11) RTV		coated: $158.3 \pm 1.5^\circ$ / $3.6 \pm 1.4^\circ$		
[20]	Aluminum foil	(1) Aluminum foil (2) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (3) Emery paper no. 400, no. 600, and no. 1000 (4) Hydrochloric acid (5) Hexadecyl-trimethoxysilane	2 wt.% hexadecyl-trimethoxy silane	$161.9 \pm 0.5^\circ/6.8^\circ$	The as-prepared SHS can effectively reduce the ice formation and is stable under indoor and ambient environments and shows good stability against water drop impact and sand-impact abrasion	The SHS fabricated by this method can mitigate the freezing process and is stable against water drop impact
[26]	Silicon	(1) Cleaning reagents (2) Acetone (3) Ethanol (4) Iso-propanol (5) NaBF_4 (6) AgNO_3 (7) PFTS (8) Water (9) Hexadecane	(1) C_4F_8 (2) SiO_x overlayers chemically modified with PFTS	(1) NanoSi + C_4F_8 : (i) 160° with H_2O , (ii) 87° with hexadecane (2) Nano-Si+ PFTS: (i) 160° with H_2O , (ii) 110° with hexadecane	–	SHS formed are highly oleophobic by this simple, electroless etching method
[29]	Aluminum alloy	(1) 2024-Al (2) KH-832 (3) Ethanol (4) H_2SO_4 , HNO_3 , H_3PO_4 (5) $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (6) CrO_3 , NaOH , Na_2CO_3 (7) $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (8) $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	Solution of KH-832 in ethanol	$167.7^\circ/5^\circ$	Surface was excellent corrosion resistant and showed stable super-hydrophobicity with WCA decreased by only 4° to 7° when kept in air for 3 months	Very stable and corrosion resistant SHS was formed
[31]	Ti6Al4V	(1) Ti6Al4V (2) FAS-17 solution (3) Acetone (4) Alcohol	FAS-17 solution	$160^\circ/3^\circ$	Corrosion resistance test showed that i_{corr} decreased by 3 times while E_{corr} increased by 0.26V	SHS formed could be used in corrosion environment

Ref. no	Substrate	Materials used	Coating materials for lowering surface energy	Max. water contact angle/ min. sliding angle	Stability	Remarks
[32]		(5) Deionized water (6) H ₂ SO ₄ (7) NaOH (8) NaHCO ₃	(No coating material used)	168 ± 7°/6°	making the SHS excellent corrosion resistant	Inexpensive, easy and environment-friendly method of fabricating SHS with good self-cleaning and corrosion-resistant characteristics
		(1) PDMS + curing agent (10:1) (2) NaCl (3) KOH, HCl (4) Deionized water (5) KCl (6) Carbon nano-powder			Excellent corrosion resistance showed when SHS was put in different pH solutions with WCA always found in range of 147°–152°	

Table 1. Chemical etching.

Both solutions were mixed into each other. After then, glass was immersed in the mixture by dip-coating process. Later, drying and heating of modified glass resulted in SHS. Both micro and nanostructures were produced on surface and WCA and SA were found to be 156° and 6° , respectively. Weight contents of SiO_2 and PTFE were also varied and then optimized to be 20:9. To check the thermal stability of coating, the temperature of reacting process varied as 100, 200, 250 and 300°C . Best super-hydrophobic features were found at 250°C after which WCA and SA kept decreasing and increasing, respectively. Fabrication procedure used was very simple and of low cost.

Fleming and Zou [15] used dip-coating method to fabricate stable super-hydrophobic and super-hydrophilic surfaces. Titanium plate was used as substrate material. Fabrication was done in three steps. In first step, grade 5 titanium substrate was sandblasted to have micro roughness on surface. Second step consisted of dipping sample into colloidal silica solution by dip-coater to generate nanoscale roughness on surface. In last step, sample was put in DRIE chamber in which C_4F_8 gas was introduced resulting in low surface energy film over the surface. WCA was found to be about 152° . Stability tests of wetting/de-wetting cycles showed that both super-hydrophilic and super-hydrophobic surfaces were stable for about 54 days. Super-hydrophilic surface fabricated by this process could be stored for about 25 months in ambient atmosphere. Liu et al. [16] used a simple one-step sol-gel process to fabricate super-hydrophobic coatings which were transparent and possessed excellent self-cleaning property due to very high WCA. The fabrication process was done on glass substrate which was initially cleaned properly. A coating solution was prepared which contained trimethoxysilane in ethanol, ammonia and deionized water. Glass substrate was immersed in that solution. Different deposition times were taken as 10, 100, 300 and 600 s and surface morphology as well WCA were observed at each deposition time. The coatings at those deposition times were named as T-1, T-2, T-3 and T-4 coatings, respectively. Surface roughness increased with increase in deposition time but decreased at 600 s deposition time. Similarly, WCA also increased with deposition time with maximum of 169° for T-3 coating and then decreased due to decrease in surface roughness. The coating showed good behavior under water-jet impact. Mechanical durability of coating was found to be poor due to softness of FAS layer. Coating also showed plastron stability.

Mahadik et al. [17] fabricated SHS by a simple and inexpensive sol-gel method. Super-hydrophobic features were achieved without using any surface modification material. Quartz substrate was used in this study which was first properly cleaned. The alcohol was prepared consisting of MTMS, methanol, oxalic acid and ammonium hydroxide. Finally, quartz substrate was dipped in the alcohol. Later on, it was annealed and dried resulting in SHS. Contact angles were measured for droplets of water, oils, acids and organic liquids. CA measurements showed very high WCA of 168° and sliding angle of 3° for double distilled water. During thermal stability tests, temperature of surface was increased to 560°C but it remained super-hydrophobic. Ultra-high water-repellent SHS was also found to be very durable. With petroleum oils, it behaved as super-oleophilic surface. Huang and Lin [18] fabricated transparent SHS by simple sol-gel process in which temperature was kept low to about 80°C . Transparent plain glass was the substrate material which was initially cleaned properly. Silicic acid was prepared from TEOS and HCl aqueous solution. It was then added to the silica/ethanol solution. Glass substrate was then dipped in the final solution for 1 min. This coated substrate was then dipped in PFOTS

ethanol solution for surface modification lowering surface energy. Silica powders used were of two sizes such as 15 and 40 nm. Surface coating varied with silica particle loading and silicic acid concentration. Best super-hydrophobic features were obtained with sample code 15B containing 0.09 M silicic acid and 6 g 15 nm silica particles. CA measurements were taken for the droplets of water as well as CH_2I_2 . For sample code 15B, contact angles for water and CH_2I_2 were found to be $160.4 \pm 4.8^\circ$ and $152.1 \pm 2.8^\circ$, respectively. Moreover, coatings fabricated in this study were also found to be stable after ultrasonication test and water-drop impact.

Ramezani et al. [19] fabricated transparent and thermally stable SHS by sol-gel process. Initially glass substrate was washed and ultrasonically cleaned. Alcohol was obtained from the mixture of ethanol, ETES and NH_4OH in right proportions. Substrate was vertically dipped in this transparent silica sol. Heating and drying resulted in the deposition of silica film over glass substrate. In last step, iso-OTMS in hexane was used as surface modification agent and its concentration varied from 0 to 15% to determine its effect on super-hydrophobicity of surface. When its concentration was 0%, WCA was found to be 108° . With increase in its concentration, WCA also increased reaching to its maximum value of 160° at 15% concentration after which no more WCA increased. The size of silica nanoparticles increased from 26 to 42 nm after modification. To determine thermal stability of SHS, temperature was increased from room temperature to 600°C but super-hydrophobicity was retained to 440°C . Moreover, SH films were highly transparent and had uniform size. Chen et al. [20] developed a simple and green methodology to fabricate SHS which have significant role in industries now-a-days. Al foil was used as a substrate followed by zinc sheet in second phase. Al foil was properly washed, cleaned and dried before applying fabrication methodology. A solution of stearic acid was made with water followed by addition of HCl in that solution. The etching process was started by dipping Al foil into the solution for 90 min, and 75 min for zinc sheet. After drying the sample, ladder-like microstructures and wave-like structures were formed on Al-etched and zinc-etched samples, respectively. WCA for both substrates was more than 150° showing super-hydrophobicity. Anti-corrosion property of SHS was also improved as compared to bare samples. The results of steam-freezing experiment showed that SHS possessed icing delay. Effect of pH on WCA of SHS was also determined and it was found that during whole range of pH 1–14, it remained higher than 150° showing stability in all conditions.

Figure 3 shows the process of solution immersion.

Wu et al. [21] fabricated SHS by one-step method which was green as well as versatile, that is, it could be applied on different types of substrates. In this method, emulsion was created in different steps beginning by dispersion of silica nanoparticles in ethanol followed by modification with PTES. Epoxy resin and curing agent were later mixed in that solution by stirring. Three different types of substrates such as wood, paper and glass were used on which SHS was fabricated. Emulsion on substrate was also coated by three methods such as brushing, spraying and dipping. The results showed super-hydrophobicity with CA around 152° and SA less than 10° on all substrates using all three methods. This acted as a proof that fabrication method is versatile and not affected by the method of coating. Epoxy resin appeared to be as a necessary ingredient for fabrication of SHS as the one formed without epoxy resin was not mechanically stable. Durability of SHS was tested by sand abrasion, knife scratching and adhesive tape tests resulting in almost constant values of CA.

Figure 3. Solution-immersion process [20].

Table 2 gives the summary of different researchers' work who have used solution immersion method for SHS fabrication.

2.3. Laser electrodeposition

Tang et al. [22] used laser electrodeposited composite method to fabricate SHS. Copper channel was used as substrate. First surface was roughed by laser, then electrodeposition was performed to obtain microstructures on surface and then dried. No coating material was used for lowering surface energy. Static WCA was found to be decreasing by increasing the channel width and the maximum WCA was 156° . Rolling angle was also determined and it was less than 5° . Moreover, the effect of microstructures on pressure drop was also studied. Pressure drop increased with increase in channel width and was also smaller in super-hydrophobic channel as compared to smooth channel. Friction factor was reduced in super-hydrophobic micro-channels by maximum of 48.8%. Li et al. [23] used a new one-step and simple idea for the fabrication of super-hydrophobic and hydrophobic surfaces. Zinc sheets were used as a substrate material. Laser ablation process was used to increase surface roughness of zinc sheet dipped in aqueous solution of H_2O_2 . Two types of laser ablation were used in the study such as nanosecond (ns) and femtosecond (fs) laser ablation. ZnO and Zn(OH)_2 were generated on the zinc surface as a result of laser ablation. Both types of laser ablation created different microstructures on surface. Clustered flower-like microstructures were formed on ns-laser ablated sample while non-directional flaky nanostructures were formed on fs-laser ablated sample. Roughness was also found to be higher for ns-laser ablated sample due to which it was super-hydrophobic with WCA and WSA of 158.5 and 4.3° , respectively. On the other hand, fs-laser ablated sample was highly hydrophobic with WCA of 145.7° and WSA of 12.5° .

Ref. no	Substrate	Materials used	Coating materials for lowering surface energy	Max. water contact angle/min. sliding angle	Stability	Remarks
[9]	Copper foams	(1) Pure copper foams (2) Acetone (3) Ethanol (4) HCl (5) Deionized water (6) Nitrogen gas (7) Ethanolic stearic acid solution	(No coating material)	156°/4°	Robust and mechanically stable	A simple one-step method, but can take longer time for fabrication of SHS
[12]	SiO ₂ -coated SiC nanowires	(1) Ethanol solution of FAS (2) Glacial acetic acid (3) SiO ₂ -coated SiC nanowires (4) Ethanol	Fluoroalkylsilane	153°	Possessed ultra-violet durability	A pure chemical approach to fabricate SHS with no change in morphology, microstructure and crystal phase
[16]	Glass substrate	(1) Glass substrate (2) Silica sol (3) Mixture of water and ethanol (4) Acetic acid (5) GPTS (6) PTFE emulsion (7) Deionized water	Modified SiO ₂ sol and PTFE emulsion	156°/6°	Coating gets destroyed as temperature is increased above 250°C	A simple and cost-effective procedure for nano-composite coating, but coating gets destroyed as temperature is increased above 250°C
[18]	Titanium surface	(1) Grade 5 titanium (2) 165-micron (3) Alumina media (4) Acetone (5) Isopropyl alcohol (6) (DI) water (7) Nitrogen (8) Colloidal silica solution (9) C ₄ F ₈ gas	C ₄ F ₈ gas	152°	High degree of stability, as surfaces retain their wetting properties for at least 54 days under multiple wetting/de-wetting cycles	An easy method of fabrication, gives long-term wetting stability and storability
[19]	Glass	(1) Glass substrates (2) Trimethoxysilane (3) Ethanol	Trimethoxysilane	169°/5°	The super-hydrophobic wetting state was preserved under the impact of a high-speed water jet,	A simple one-step process to fabricate optically transparent SHS with very high contact angle

Ref. no	Substrate	Materials used	Coating materials for lowering surface energy	Max. water contact angle/min. sliding angle	Stability	Remarks
[21]	Quartz substrates	(4) Ammonia (5) Deionized water (1) Quartz substrates (2) Methyl-trimethoxysilane (MTMS) (3) Methanol (99%) (4) Hexane (85%) (5) Oxalic acid (6) Liquor ammonia (7) pH indicator papers 1–14	(No coating material used)	$168 \pm 2^\circ/3 \pm 1^\circ$	however, the coating showed poor mechanical durability When MTMS based coating was exposed with outdoor temperature, wind, air and humidity variations over six months environment, the coating showed reduced water contact angle by 27° , and increased sliding angle $8 \pm 1^\circ$	of 169° but mechanical durability is poor A simple and inexpensive method to fabricate SHS with very high WCA on quartz substrate without surface modification
[22]	Transparent plain glass	(1) Transparent plain glass (2) Tetraethoxysilane (TEOS) $C_8H_{20}OSi$ (3) Hydrochloric acid (HCl) (4) Ethanol (C_2H_5OH) (5) Silica powder, 40 nm and 15 nm, SiO_2 (6) 1H,1H,2H,2H-perfluorooctyltrichlorosilane, PFOTS, $CF_3(CF_2)_5(CH_2)_2SiCl_3$	1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane, PFOTS, $CF_3(CF_2)_5(CH_2)_2SiCl_3$	(1) For water, $160.4 \pm 4.8^\circ/7.1 \pm 2.0^\circ$ (2) For CH_2I_2 , $152.1 \pm 2.8^\circ/84.5 \pm 9.3^\circ$	Coating was chemically and mechanically stable as tested by ultrasonic damage and water dropping impact	SHS fabrication process was conducted by a wet chemical technique at relatively low temperature conditions
[23]	Glass substrates	(1) Glass substrates (2) Ethanol and hexane (3) Ethyl-triethoxysilane (4) Isooctyl-trimethoxysilane (5) Ammonia (6) Deionized water	Isooctyl-trimethoxysilane (iso-OTMS)	160°	The SH silica films are thermally stable up to $440^\circ C$ and above this temperature, the silica films lose super-hydrophobicity	Transparent and thermally stable films are fabricated by this method
[33]	(1) Aluminum foil (2) Zinc sheet	(1) Al foil (2) Zn sheet (3) Ethanol (4) Acetone (5) Hydrochloric acid (6) Stearic acid (7) Deionized water	(No coating material used)	$>150^\circ$ for both Al foil & Zn sheet	SHS showed excellent stability when put in acidic and basic conditions with WCA always more than 150° . Also great corrosion protection was found	A facile and green method to prepare very stable and corrosion resistant SHS

Ref. no	Substrate	Materials used	Coating materials for lowering surface energy	Max. water contact angle/min. sliding angle	Stability	Remarks
[35]	(1) Wood (2) Paper (3) Glass	(1) Wood sample (2) Filter paper (3) Glass (4) Silica nanoparticles, 12 nm (5) PTES (6) Epoxy resin & curing agent (E-44) (7) Absolute ethanol	PTES	~152°/10° for all SHS	SHS formed were mechanically very durable when tested by finger wiping, tape peeling and sandpaper abrasion and maintained their super-hydrophobicity in solutions of different pH	A green, versatile, one-step method independent of substrate to fabricate very durable SHS

Table 2. Solution immersion.

Chun et al. [24] developed fabrication method of SHS on copper substrate and the focus of this study was kept to the fast fabrication of SHS. First, copper substrate was exposed to the nanosecond laser beam originating from laser beam machining of 3.3 watt power and 20 Hz frequency. Earlier before this study, it had already been found that laser beam produced layer of CuO on sample which was hydrophilic and it took a long time about 27 days to be converted into SHS which had Cu₂O on the surface. So, instead of keeping the laser textured surface in ambient conditions, it was made super-hydrophobic using annealing at low temperature, that is, 100°C. This accelerated the conversion of CuO into Cu₂O resulting in the formation of SHS after 13 h. As copper is also stable with ethanol, so additional reduction in time to get SHS was achieved when ethanol was used by which SHS was formed in less than 5 h. WCA was also found to be maximum of 165° showing super-hydrophobicity.

Figure 4 shows the schematic illustration for fabrication of SHS by laser beam machining.

Table 3 summarizes the work of different researchers who have used electrodeposition technique for SHS fabrication.

2.4. Template deposition

Wang et al. [25] used template deposition method for the fabrication of SHS using copper sheet as substrate. The fabrication method consisted of three steps. First step was to prepare template from polystyrene microspheres powders. Second step was to put copper plate in polystyrene colloidal microspheres with CuSO₄ solution as an electrolyte. The electrodeposition potential was about −0.5 V and SEM images were taken after deposition time of 19 s. During this process, copper atoms filled the voids in the template. In final step, surface was modified using fluorosilane solution resulting in a SHS. WCA of 5 µL droplet was measured to be 156.3°. WCA increased with increase in deposition time to 19 s and then decreased after that. Bhagat and Gupta [26] developed a purely physical process of fabricating super-hydrophobic polycarbonate surfaces (PC). Silicon wafers were used as substrate which along-with PC were initially washed and cleaned properly. In first step of fabrication, micro-textures were produced on substrate by high power laser and in second step, those microstructures were thermally replicated on PC surface by sandwiching them between two hot plates having different temperatures. Upon cooling, both surfaces were then separated from each other. Effect of replication temperature was such that when temperature varied from 155 to 175°C,

Figure 4. Schematic illustration of SHS with laser beam machining and post-process [24].

Ref. no	Substrate	Materials used	Coating materials for lowering surface energy	Max. water contact angle/ min. sliding angle	Stability	Remarks
[5]	Copper	(1) Copper channel (2) Solution of CuSO_4 and HCl as electrolyte (3) Flat copper as anode (4) Ethyl glycol	(No coating material used)	$156^\circ / <5^\circ$	–	A method to fabricate SH copper channels without the use of coating material
[30]	Zinc sheet	(1) Zinc sheet (2) Hydrogen peroxide aqueous solution	(No coating material used)	(1) ns-laser ablated sample: $158.5^\circ / 4.3^\circ$ (2) fs-laser ablated sample: $145.7^\circ / 12.5^\circ$	–	One-step and simple method with small number of materials needed
[37]	Copper	(1) Pure copper plate (2) Ethanol	(No coating material used)	$165^\circ / 9^\circ$	–	Method to fabricate SHS with reduced time to gain super-hydrophobicity after laser texturing

Table 3. Laser electrodeposition.

micro-pillars formed on PC surface varying in the average height from $1.34\text{ }\mu\text{m}$ to $6.68\text{ }\mu\text{m}$. During this, WCA also varied from 82° to maximum 155° . Super-hydrophobic PDMS surfaces were also fabricated by this process with maximum CA of 162° . This physical process of fabrication resulted in robust SHS with good mechanical properties.

Figure 5 shows schematic diagram for the fabrication of super-hydrophobic PC by electrodeposition.

Liu et al. [27] prepared SHS by simple, rapid and facile method. SiC paper was first sonicated, rinsed with ethanol and then baked. PDMS pre-polymer was pored over SiC paper. It was peeled from PDMS cast after cooling. As rough PDMS was templated from SiC paper, flat PDMS was also templated in the same way on Si wafer. The WCA for both cases were measured and it was found that rough PDMS behaved as super-hydrophobic while flat PDMS showed hydrophobic behavior with WCA of 154° and 113° , respectively. SHS formed was also found to possess excellent adhesive properties described by hybrid wetting state.

Table 4 gives the summary of different researchers' work who have used template deposition method for fabrication of SHS.

2.5. Spray coating

Momen and Farzaneh [28] fabricated exceptionally stable SHS using a simple and cost-effective approach of spray coating. Glass substrate used was first ultrasonically cleaned followed by preparation of three separate samples. First sample 'a' consisted of RTV silicon

Figure 5. Schematic diagram for fabrication of super-hydrophobic PC by laser micro-texturing of Si wafer and its subsequent replication [26].

rubber (SR) in hexane, sample 'b' of ZnO nanoparticles in hexane and SR while sample 'c' contained both ZnO and SiO₂ nanoparticles in hexane and SR. Then all three samples were separately spray-coated on glass slides by using spray gun. SEM investigations showed that sample 'a' coating resulted in smooth surface. Sample 'b' coating caused nanoscale roughness on surface while sample 'c' coating resulted in both micro and nanostructures. WCAs for all samples a, b and c were measured to be 117.3, 132.5 and 162.7°, respectively. Different stability tests carried out on SHS resulted in slight decrease in WCA after 10 days by immersing in different pH solutions. UV and humidity had also little effect on WCA. Against heating treatment at 150°C for almost a month, WCA was decreased just a little showing the stability of SHS. Ipekci et al. [29] developed one-step spray-coating method of fabricating SHS which had improved mechanical robustness and durability. A matrix was required for better dispersing of silica nanoparticles functionalized with fluorinated silanes. Hydroxyl-terminated polystyrene was used as a matrix which reacted with substrate to form polymer brushes through covalent bonding. Glass slides were used as a substrate. WCA measurements showed that CA was greater than 170° and SA was approaching 0°. WCA was highest for weight-ratio of 1 between PS-OH and FNP. Effect of curing temperature was also determined and WCA was found to be maximum at 190°C. Abrasion tests also showed that WCA decreased after grain velocity of 10 km/h. SHS formed were also transparent to 85%. Enhancement of mechanical robustness was different for different substrates and polymers.

Ref. no	Substrate	Materials used	Coating materials for lowering surface energy	Max. water contact angle/ min. sliding angle	Stability	Remarks
[8]	Copper	(1) Copper sheet (2) Acetone (3) Styrene (4) Sodium dodecyl sulfate (5) Ethanol (6) Deionized water	Fluoroalkylsilane	156.3°	–	The procedure consists of three steps, that is, template preparation, electrodeposition and surface modification
[11]	Polycarbonate surface	(1) Silicon wafers (2) Acetone (3) Methanol (4) Deionized water (5) Polycarbonate sheet (6) PDMS sheet	(No coating material used)	(1) For micro-textured PC: 155°/<10° (2) For micro-textured PDMS: 162°	The micro-textured PC surfaces are robust enough and exhibit very low damage to the master	A simple physical method to make SH PC surface without any chemical change
[25]	PDMS	(1) PDMS (2) SiC paper (3) Deionized water (4) Formamide, 99.5% (5) dimethyl sulfoxide (DMSO), 99.8% (6) Ethanol	(No coating material used)	153°/23°	Water drop test, ultrasonic treatment and water immersion tests show the high durability of SHS, also thermally stable below 500°C	A simple, inexpensive and modification-free process of fabricating highly durable, transparent, thermally stable SHS

Table 4. Template deposition.

Wang et al. [30] fabricated SHS by cost-effective and environment-friendly method. The method used was salt-spray method which increased surface roughness, followed by modification of surface reducing its surface energy. Two substrate materials such as steel and Mg alloy were separately used. Both substrates were first properly polished, cleaned and then dried. These were placed for about 2 h in the neutral spray chamber which contained NaCl solution creating humid and fog condition. This generated needle-like structures on steel and flower-like structures on Mg alloy surface. Finally, super-hydrophobicity was achieved when above samples were put in solution of FAS-17. WCA measurements showed that CA of 156.05 and 152.65° while SA of 2 and 5° were achieved for steel and magnesium alloy samples, respectively. Mechanical durability of SHS formed was tested by water fall test in which kinetic energy of falling water varied. The results showed that WCA decreased after 20 minutes but water-repellent properties still remained in the solution. Although durability of SHS formed by this method was not excellent, it is still good.

Figure 6 shows the schematic diagram for fabrication of SHS by salt-spray method.

Table 5 summarizes the work of different researchers who have used spray coating technique for SHS fabrication.

Figure 6. Schematic diagram for fabrication of SHS by salt-spray method [30].

2.6. Other techniques

Feng et al. [31] fabricated SHS using a simple method in which copper plate was used as a substrate material. Fabrication process was completed in three steps. First, copper powder was oxidized with $AgNO_3$ solution after it was ultrasonically cleaned with nitric acid and distilled water. Second, surface hydrophilicity was changed into hydrophobicity by lauryl mercaptan (DM). In last step, mold compression was performed on copper powder under 80 MPa to obtain super-hydrophobic characteristics. Tests showed maximum WCA of 155.2° and SA was also less than 5° . Super-hydrophobicity of surface was also dominant for other fluids. Copper-based SHS was also found to be very long-term durable, storable, regenerable and of excellent cleaning property.

Sun et al. [32] developed composite electro-brush flow plating technology for the fabrication of SHS over copper substrate. Experimental device was made at first which consisted of tank, linear motor, pump, substrate cathode, steel anode, plating solution, etc. Copper plate was polished mechanically, ultrasonically cleaned and then fixed in experimental device. Ni plating solution consisted of thoroughly mixed nano- Al_2O_3 particles was prepared. Electro-brush was moved reciprocally by motor to rub the substrate surface. Finally, n- Al_2O_3 /Ni coating was obtained on copper surface with micro-nanostructures. The resulting sample was immersed in FAS solution for surface modification. The results showed WCA of 162° and SA of less than 10° . The WCA increased with increasing plating voltage to 12 V and then decreased after it. Similarly, WCA increased with plating time to 2 s and then remained almost constant. Final SHS obtained possessed excellent mechanical properties and stability.

Huang and Leu [33] used spin coating method to fabricate SHS. Substrate used was copper heat sink. Fabrication process was completed in three steps. In first step, chemical polishing was done on substrate to remove oxides and impurities. In second step, CuO nanostructures were produced on substrate surface by immersion in H_2O_2 solution. In last step, electronic liquid EGC-1720 was prepared by fluorosilane polymer and hydrofluoroether solvents. Sample was placed on acrylic cylinder resulting in SHS after spin coating. WCA was measured to be $153.43 \pm 5.13^\circ$. Comparison of pure copper heat sink and super-hydrophobic copper heat

Ref. no	Substrate	Materials used	Coating materials for lowering surface energy	Max. water contact angle/min. sliding angle	Stability	Remarks
[17]	Glass slide	(1) Glass substrate (2) RTV silicon rubber (3) Hexane (4) ZnO nanoparticles (5) SiO ₂ nanoparticles (6) Acetone (7) Water (8) Nitrogen gas	SR/ZnO/SiO ₂ composite	162°/7°	Coating possesses (1) Medium-good stability against a wide range of pH solutions (2) No significant effect of UV and humidity (3) Retained its super-hydrophobic and roll-off properties against the heating treatment	A simple spray-coating method in one-step process, ultra-water-repellent properties in several environmental factors
[27]	Glass slide	(1) Glass slides (2) Polystyrene (PS) (3) hydroxyl-terminated polystyrene (PS-OH) (4) Toluene (99%) (5) Cyclohexane (HPLC grade, 99.9%) (6) Silica NPs (12 nm diameter) (7) FDTs	Fluorinated silanes	170°/0°	(1) For impact velocities lower than 10 km/h during sand abrasion tests, surfaces retained their super-hydrophobicity (2) Surfaces were transparent with 85% light passing capability	Mechanically robust and transparent SHS was formed by one-step spray-coating method
[36]	(1) Steel (2) Magnesium alloy	(1) Mg alloy (2) Low carbon steel (3) Ethanol (4) Acetone (5) Sand paper (6) NaCl (7) Deionized water (8) 1 wt% FAS-17	1 wt% FAS-17	(1) For Mg: 152.65°/5° (2) For steel: 156.05°/2°	Waterfall jet test at 100 kPa showed that WCA and sliding angle started decreasing and increasing, respectively, after 20 min, so moderate durability was found	Cost-effective and environment-friendly method to fabricate SHS with moderate durability

Table 5. Spray coating.

sink was also carried out by performing CHT experiments. Surface coating was degraded during CHT experiments due to continuous heating by condensate water droplets.

Zhang et al. [34] fabricated anti-corrosive and durable SHS by dual-layer method. Glass slide was used as substrate material which was properly cleaned. The fluorinated silica was prepared and mixed with PFTS under stirring to get final fluorinated silica. Then PDMS solution was mixed with fluorinated silica and layer 1 was obtained by its spray coating on glass substrate. After then, layer 2 was obtained by spray coating of fluorinated silica on top. Micro-protrusion structured surface was obtained whose WCA was found to be maximum at 157°. Positive results from the surface abrasion test and ultrasonication test showed mechanical stability of super-hydrophobic coating. SHS also showed anti-corrosive behavior when copper substrate was used. Moreover, immersion in different pH solutions also did not change super-hydrophobicity of surface fabricated in this study.

Stanton et al. [35] prepared SHS by simple and cost-effective method. Glass substrate was used which was dip-coated into the already prepared PDMS solutions. These PDMS films were exposed to the candle flame. Candle soot made the films black. Removal of candle soot then resulted into the formation of nanostructures on the films and transparency was also obtained. Then, calcination was performed in muffle furnace at 450°C to obtain SHS. Transmittance of SHS was affected by calcination temperature and dip-coating times. Transmittance was found to be maximum at 450°C. Three tests including water-drop test, ultrasonic treatment and water immersion were conducted to check the durability of obtained SHS. Tests showed that SHS were very durable and could easily recover super-hydrophobicity after heat treatments. WCA and SA were measured to be as 163 and 1°, respectively.

Fabrication of SHS requires roughness of surface followed by lowering surface energy. Song et al. [36] used silicon substrate for fabrication of SHS. Surface was made textured by the Al-induced crystallization of amorphous silicon. Lowering of surface energy was done by the deposition of OTS coating. WCA increased by both roughing surface and then by lowering its energy. Only lowering the surface energy of silicon without modifying surface structure resulted in less increase in WCA. OTS-modified textured surface showed maximum CA angle of 155° while OTS-modified smooth surface showed only 112°. Adhesion and friction performance of SHS also decreased by texturing the surface. So, it was obvious that although both texturing as well as surface modification caused increase in WCA along-with decrease in adhesion and friction but texturing played a greater role in this. Sun et al. [37] fabricated SHS on Al substrate by a facile and scalable method. Al foils were first pre-treated in which oxide layer over their surface was completely removed. Then sample was cleaned, rinsed and finally dried. Chemical etching was done by dipping pre-treated samples in HCl solution for 5 min. The chemically etched sample was then placed over stainless steel mesh in a crucible pot containing PDMS solution. The calcination of PDMS at 300°C resulted in decomposition and oxidation reactions on PDMS producing organic SiO₂ nanoparticles. These PDMS vapors grew on chemically etched Al surface leading to surface roughness as well as lowering of surface energy. This combined methodology of chemical etching and chemical vapor deposition produced SHS on Al with WCA reaching 158.7°. The polarization curves showed increased corrosion resistance of super-hydrophobic Al surface. SHS formed were also capable of self-cleaning.

Table 6 gives the summary of different researchers' work who have used other techniques for fabrication of SHS.

3. Heat transfer and other applications

Super-hydrophobic surfaces play a significant role in various heat transfer applications in which surface morphology is very important. In boiling, super-hydrophobic spots along-with hydrophilic spots can result in very high critical heat flux and heat transfer coefficient (HTC) values. Similarly, SHS in condensation heat transfer (CHT) experiments leads to drop-wise condensation in which more than 10 times heat transfer coefficients can be achieved as compared to that in film-wise condensation. Long term-stability and storability are the key parameters to focus on while using SHS for condensation. Another important application of SHS is

Ref. no	Technique used	Substrate	Materials used	Coating materials for lowering surface energy	Max. water contact angle/min. sliding angle	Stability	Remarks
[6]	Compression molding	Copper	(1) Copper powder (2) AgNO ₃ (3) HNO ₃ (4) Lauryl mercaptan (DM) (5) Ethanol	Lauryl mercaptan (DM)	155.2°/<5°	Remained stable when (1) Placed in the air for ten months (2) Soaked in water for half a month (3) For over a wide pH range (i.e. pH = 6–14)	A simple method to fabricate SHS with long-term durability, stability, storability regenerability and self-cleaning property
[10]	Flow plating technology	Copper plate	(1) Pure copper plate (2) Fluoroalkylsilane (3) Nano-particle n-Al ₂ O ₃ (4) Nickel plating solution reagent	Fluoroalkylsilane	162°/ <10°	Outstanding mechanical properties and stability	A method to fabricate very stable SHS and greater contact angle but also greater sliding angle
[14]	Spin coating	Pure copper heat sink	(1) Pure copper heat sink (2) HNO ₃ solution (3) H ₂ O ₂ aqueous solution (4) EGC – 1720 (fluorosilane polymer + hydrofluoroether)	EGC – 1720 (fluorosilane polymer + hydrofluoroether)	153.43 ± 5.13°	EGC-1720 can withstand a harsh vapor environment and is durable for 100 h	A concise and low-cost surface modification method but not much durable
[15]	Dual-layer method	Copper surface	(1) Silicon dioxide nano-powder (2) PFTS (3) Polydimethyl-siloxane		158.7°	SHS were mechanically durable with WCA always greater than 150° after abrasion, ultrasonication and immersion in different pH solution tests. SHS was also found very corrosion resistant	Highly stable and corrosion-resistant SHS was produced by this method
[24]	Calcination process	Glass substrate	(1) Glass slides (2) Wax (3) Cotton threads (4) α , ω -dihydroxypolydimethylsiloxane (5) TEOS	(No coating material used)	163°/1°	–	A rapid, reproducible technique to fabricate very adhesive SHS

Ref. no	Technique used	Substrate	Materials used	Coating materials for lowering surface energy	Max. water contact angle/min. sliding angle	Stability	Remarks
[28]	Chemical vapor deposition	Silicon	(6) Dibutyltindilaurate (DBTDL) (7) Ethanol and n-hexane (8) <i>n</i> -dodecane (1) Silicon wafers (2) Acetone (3) Iso-propanol (4) Deionized water (5) Aluminum etchant—type D (6) Octadecyltrichlorosilane (OTS)	Octadecyltrichlorosilane (OTS)	155°/1°	SHS formed had adhesiveness and COF reduced upto 90 and 75%, respectively	This method produced SHS with good adhesive and frictional characteristics
[34]	Chemical vapor deposition	Aluminum foil	(1) Al foil (2) SiC paper (3) NaOH solution (4) HCl solution (5) PDMS (6) Deionized water	(No coating material used)	158.7°	SHS showed excellent corrosion resistance in 3.5% NaOH solution	Facile method to fabricate corrosion-resistant SHS with good self-cleaning ability

Table 6. Other techniques.

anti-icing or anti-frosting which is the primary requirement for PV cells, airplanes, power lines, ships, etc. Moreover, drag reduction characteristics of SHS have also been discussed in this section, which are important for the submarine outer surfaces as well as internal surface of tubes during internal flow.

3.1. Boiling

Betz et al. [38] explained the effect of surface morphology on boiling heat transfer. The density of active nucleation sites and size of contact diameter of departing droplets are important parameters to obtain minimum heat flux (MHF) in boiling. For MHF, number of active nucleation sites should be maximum which can be obtained using hydrophobic surface and contact diameter should be smallest to maintain water transport to hot surface as in hydrophilic surface. Using a single type of surface could fulfill one criterion but not the second one, thereby reducing maximum heat flux. In this study, it was determined that surface having characteristics of both hydrophobic and hydrophilic surface showed CHF more than that obtained by using individual surfaces. This surface was named as biphilic surface for which maximum heat transfer coefficient was two and four times higher than hydrophilic and hydrophobic surface, respectively. Hydrophobic regions in biphilic surface increased the number of active nucleation sites while hydrophilic regions decreased the contact diameter, thereby aiding in liquid transport to hot surface.

Malavasi et al. [39] performed boiling heat transfer experiments on surfaces with various topographies to find the effect of roughness and wettability on boiling regimes. Six different types of surfaces (including two hydrophilic, one hydrophobic and three SHS) were prepared using stainless steel as substrate material. Shape of boiling curve for SHS was different from the typical boiling curve in sense that onset of nucleate boiling (ONB) was achieved near 0°C ($<5^{\circ}\text{C}$) and Leidenfrost point was also reached earlier just after ONB. Due to more roughness of SHS, number of nucleation sites was also higher, so bubbles formation started just after T_{sat} leading to early ONB. Due to large number of vapors formed on surface, heat transfer to liquid started decreasing rapidly leading to early Leidenfrost point. It was also found that although all three SHS had different roughness values, but due to almost same WCA, all showed same boiling curves. Hence, wettability was dominant over roughness for any surface whose CA exceeded 135° which is the case of SHS.

Yamada et al. [40] created biphilic surfaces on copper substrate and compared it with plain copper surface during nucleate boiling process at pressure values ranging from atmospheric to 6.9 kPa. Difference of ONB between biphilic and plain surface increased with decreasing pressure. Higher HTC values were obtained for biphilic surface than plain surface at low pressure values showing enhanced efficiency of biphilic surfaces at sub-atmospheric pressure. However, this efficiency enhancement was not found below transition pressure at which continuous boiling converted into intermittent boiling. Effects of diameter and pitch of hydrophobic spots on biphilic surface were also investigated by testing three samples. At low heat flux, increasing hydrophobic spot diameter and reducing pitch led to more HTC while at low heat flux, smaller diameter with increased number of spots showed high HTC while pitch affected less.

Fan et al. [41] investigated the effect of four surfaces such as super-hydrophilic (0°), hydrophilic (23°), hydrophobic (119°) and super-hydrophobic (164°), on transient pool boiling by quenching methods. In quenching process, temperature was decreased and its decreasing rate was affected by the nature of surface. Cooling rate was found to be decreasing with increasing WCA. The reason for lowest cooling rate for SHS was the retention of vapor film on surface. On the other hand, super-hydrophilic surface showed maximum wettability leading to the collapse of water film. Boiling curves showed that CHF was found maximum for super-hydrophilic surface at higher values of superheat. Again the reason found was deterioration of vapor film at higher superheat.

3.2. Condensation

Kim et al. [42] investigated the effect of super-hydrophobicity of TFE-coated Pyrex glass tube and compared it with bare tube by conducting condensation experiment. Steam was produced by steam generator and then passed through 3 m long and 19 mm diameter glass tube inclined at $3\text{--}5^\circ$ and finally collected as liquid at downstream. Air was cross-flowed through bare tube first and then through internally TFE-coated tube. Wall temperature distributions were taken for both cases. Flow regimes were also studied. In bare tube, condensation was film-wise and flow regimes were fully stratified while in TFE-coated tube, liquid droplets were formed on inside of tube. Averaged local heat flux values were higher for TFE-coated tube to 2 m length while lower or almost same in the remaining tube length. Temperature values at wall were higher for TFE-coated tube for the whole tube length due to the presence of droplets at inside wall instead of film. In the downstream region, local heat flux values were reduced due to increase in vapor quality. Overall, TFE-coated tube showed greater heat flux due to drop-wise condensation as compared to bare tube with film-wise condensation.

Lu et al. [43] fabricated super-hydrophobic Si nanowires through electroless etching and compared it with hydrophobic Si wafer during condensation process. Test samples were placed in experimental system where T_{sat} was kept constant at 80°C and pressure at 47 kPa. Heat transfer coefficient (HTC) and heat flux were determined for sub-cooling values to 20 K. Flooding was observed in case of hydrophobic Si but super-hydrophobic Si showed droplet jumping and efficient shedding without flooding. At low sub-cooling (1 K), the difference between HTC values of SHS and hydrophobic Si was very large as compared to the difference at high sub-cooling (15 K). This decrease was due to the increased surface coverage ratio of droplets at tube that acted as a resistant to heat transfer. Coverage ratio, departure diameter and departure frequency of water droplets were also found to be increasing with increase in sub-cooling.

Yin et al. [44] prepared three different types of super-hydrophobic coatings such as PFO, PA and RTC coatings with WCA 162 , 161.7 and 158.3° , respectively, onto glass substrate through chemical etching method. All three types of coated substrates were put in different condensing environments. These included temperature values varying from 30°C to -10°C at each of the RH values 30, 60 and 90%. At 30% RH, all the coatings showed negligible changes in WCA values. But at 60% RH and -10°C , PFO, PA and RTC coating showed declined values of WCA as 148 , 148 and 130° , respectively. A relatively more decreasing trend of WCA was found with 90% RH when all coatings lost their super-hydrophobicity with RTC coating showing the maximum decline in WCA to 114.7° . On the other hand, SA for each coating was found to be

increasing with increase in RH values and decrease in temperature, showing considerable super-hydrophobicity loss.

Bisetto et al. [45] compared CHT on hydrophilic and super-hydrophobic copper substrates with WCA 86 and 159° values using thermosyphon two-phase test rig. SHS had micro-nanostructures which brought water molecules in Cassie-Baxter state due to entrapped air after condensation leading to the increased mobility of droplets. Higher droplets departure rate resulted in increased heat transfer for SHS. Effects of vapor velocity and wall sub-cooling on heat flux as well as heat transfer coefficient were also investigated. HTC and heat flux increased with increasing vapor velocity while the effect of wall sub-cooling was not much significant. Drop-wise condensation was observed on SHS for repeated experiments in 5 working days after which DWC transited into FWC with heat transfer performance even more worse than on hydrophilic copper substrate.

3.3. Anti-icing

Liu et al. [46] examined the anti-icing property or freezing delay of SHS. Freezing delay between bare (B) and SHS was also compared. 7075 Al alloy was used as a substrate material. Through laser processing and modification, SHS on substrate was fabricated. Three different types of microstructures, that is, round hump (R), square protuberance (S) and mountain-range-like structure (M) were generated with microstructure 'M' showing maximum WCA of $166 \pm 2^\circ$. To check anti-icing property of all types of SHS as well as bare surface, an apparatus was developed. Testing samples were placed on experimental plate whose temperature was reduced from 16°C to -15°C at a rate of 0.2°C/s. Experimental plate was tilted at 5° and water was sprayed at testing sample. The freezing times of B, R, S and M were found to be as 319, 1153, 1165 and 1938 s, respectively. M surface showed maximum freezing delay indicating that with increasing WCA, freezing time of water droplet was also increased. So, type of microstructure on surface played the key role in freezing delay. Model was also established in this study by which heat transfer between droplet and surface could be easily analyzed.

Kim et al. [47] applied stochastic approach for the determination of freezing delay of water droplet on bare and SHS. At first, SHS on Al 6061 was prepared by etching and surface modification. Then test sample was placed indirectly on thermoelectric element (TEC) with thermocouples and camera for observation. Temperature of TEC decreased from 25°C to -10°C at a rate of 10°C/min. Ice nuclei started growing near the surface, so thermocouples were also immersed in droplet near the surface for precise measurements. Temperature of every droplet on both bare and SHS was measured during cooling and super-cooling periods. For both bare and SHS, freezing delay points showed random distribution. By using better approach of stochastic data analysis instead of arithmetic average, it was found that freezing delay for SHS was three times more than that of bare surface showing anti-icing behavior of SHS.

Wang et al. [48] prepared three types of samples: sample 1 (bare Al, WCA = 86°), sample 2 (Al with nanostructures, WCA = 156°) and sample 3 (Al with micro-nanostructures, WCA = 160°) and compared their anti-icing characteristics by placing water droplet of 4 µL on each sample at -15°C. Freezing delay time for sample 1, 2 and 3 were 99, 1176.9 and 3942.1 s, respectively.

The presence of micro-nanostructures on sample 3 decreased solid/liquid area fraction which led to the maximum freezing delay. The results of frost formation measurements at 28°C and relative humidity 78% for all three samples showed frosting time of 81, 75 and 51 min, respectively. Again the roughness factor led to maximum frosting time for sample 3. Zuo et al. [49] prepared SHS on glass with ZnO nanorods and compared its anti-frosting characteristics with permanent room temperature vulcanized (PRTV)-coated glass and bare glass. Frosting process was investigated on all three surfaces using Peltier-based platform in which samples were maintained at three different temperatures: 0, −5 and −10°C. At −5°C, frost was formed on bare glass, PRTV-coated glass and SHS glass after 24, 43 and 153 min, respectively. This showed the prolonged delay for SHS compared to bare glass and PRTV-coated glass. At 0 and −10°C, SHS again showed frosting delay leading to the excellent anti-frosting performance of SHS. The reason for this delay was that nanorods in SHS increased the air cavities between solid surface and liquid droplets. This promoted self-transfer movement of condensed droplets and inhibited frost formation. Also, the SHS showed extreme durability after 30 cycles of frosting/defrosting process with WCA decreasing from 167 to 162° only.

Liu et al. [50] prepared SHS using fiberglass cloth (FC-coated SHS) on Al substrate and compared its anti-icing characteristics with bare Al surface (bare-Al). The testing device used consisted of container with low temperature environment (−35°C), air-blast atomizer to spray cold air, sample holding device tilted at 30° with electric heaters embedded. Without electrical heating, FC-coated SHS showed excellent ice formation delay with only 24% surface with accumulated ice at time when bare-Al was completely covered with ice. During electrical heating case, applied voltage varied as 5, 7, 7.4 and 10.8 V to find the power at which no ice could accumulate on both surfaces. At all voltages, ice accumulation on FC-coated SHS was always less than that on bare-Al and the voltages at which no ice accumulated on FC-coated SHS and bare-Al were 7.4 and 10.8 V, respectively, showing more icing delay for FC-coated SHS. As a result, 51% energy saving to inhibit icing on FC-coated SHS was determined.

3.4. Drag reduction

Lv and Zhang [51] fabricated SHS on Al alloy and examined its drag reduction and heat transfer characteristics by turbulent flow of water in counter-current tube-in-tube heat exchanger. Bare Al and SHS tubes were used as inlet tubes separately. Inlet tubes of three different diameters: 4, 8 and 12 mm were investigated and their corresponding drag reduction values were found to be in range of 12.4–17.8%, 8.3–13.1% and 8.3–12.8%, respectively. Drag reduction increased with decreasing inlet tube diameter due to increasing area fraction of air-liquid interface. Effect of Reynolds number on drag reduction was also determined. At low Re, drag reduction was higher due to dominance of air-liquid interface causing slip flow while at high Re, turbulence replaced air in air-liquid interface with water, thereby decreasing drag reduction. Due to slip flow, friction factor as well as pressure drop were also less in SHS tube as compared to bare Al tube. Moreover, as air in air-liquid interface acted as insulator, HTC suppressed in SHS was compared to bare tube. To check overall performance of SHS, performance evaluation criterion (PEC) was determined for all three SHS tubes. For all values of Re, 8 and 12 mm tube showed PEC >1 while 4 mm tube showed PEC <1 after Re = 6800.

4. Conclusion

This chapter summarizes different techniques for the fabrication of super-hydrophobic surfaces. In each technique, micro-nanostructures are produced on the substrate surface due to which surface wettability is reduced to a great extent. The water droplets on such surface appear in Cassie-Baxter state in which they have almost spherical shape and very high mobility. This feature of super-hydrophobic surface has a great use in various heat transfer applications like boiling, condensation, anti-icing, drag reduction, etc. where high heat transfer coefficients, icing delay time, energy saving, friction reduction are the important parameters. The future challenge is to fabricate super-hydrophobic surfaces which have long-term stability and storability.

Nomenclature

SHS	Super-hydrophobic surface
WCA	Water contact angle
CAH	Contact angle hysteresis
FAS	Flouroalkyl silane
CA	Contact angle
SA	Sliding angle
RH	Relative humidity
PTES	1H,1H,2H,2H-perfluorooctyltriethoxysilane
PDMS	Polydimethyloxysilane
WSA	Water sliding angle
FNP	Fluorinated silica nanoparticles
CHT	Condensation heat transfer
PFTS	1H,1H,2H,2H-perfluorooctyltriethoxysilane
OTS	Octadecyltrichlorosilane
MHF	Minimum heat flux
CHF	Critical heat flux
TFE	Tetrafluoroethylene
DWC	Drop-wise condensation
FWC	Film-wise condensation
PEC	Performance evaluation criterion

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