An Overview of Superamphiphobic Materials

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Abstract

The word superamphiphobicity refers to the effect in which the techniques of surface chemistry and surface-roughness in order to make the surface superhydrophobic and superleophobic, both sharing the criteria of contact angle greater than 150^0 along with lower contact angle hysteresis. In this review, we have recapitulated the modification of the surface, selection of substrates and fabrication methods that lead to superamphiphobicity and their characters that lead to functional applications.

Keywords: Superamphiphobicity, Superhydrophobic, Superleophobic, Vitality, Nano scale Roughness

1. Introduction:

Extensive research interest has been observed in the field of superamphiphobic surfaces that are man-made. In a wider view nature provides us a variety of plant leaves, insect legs, and wings that are superamphiphobic. Contact angles larger than 150^0 and sliding angles less than 10^0 formulate the concoction of superamphiphobic coatings. Superamphiphobicity provides excellent outcomes in self - cleaning, anti-fouling, anti-bacterial, gas sensing, oil or water separation and droplet manipulation properties [1]. Wettability of a solid surface is determined by two factors, nature and its structure. Previous studies have found that constructing appropriate hydrophilic regions on superamphiphobic surfaces would promote nucleation and self-repelled jumping has become an important way to remove water droplets from the surface [2]. There are two major approaches to construct superhydrophobic surfaces over a solid surface [3-5].

i) By modifying a lower surface energy substance on a rough surface
ii) By increasing the roughness of the surface of the low surface energy substance[6, 7]

Modifying a surface with low surface energy groups can effectively increase its water as well as oil contact angles and roughening is another methodology to enhance the wettability of a surface. Xiaolong et.al put forth that superamphiphobicity can be approached in one step with Multiwalled carbon Nanotube with a coralline structure [8]. The terminologies superomniphobic and superamphiphobic were used to describe the nature of these surfaces both superhydrophobic and superoleophobic. Superleophobic surfaces were achieved by introducing a third factor, re–entrant curvature structure and it also resembles a overhanging structure reported by Cohen et.al and Gao .et.al respectively [9, 10] whereas the cooperation of micro or nano scale heirarchial structures with low surface energy materials has been the most important strategy for fabricating superhydrophobic surfaces [11].

1.1 Approach towards the generation of Superamphiphobic Surfaces:

A combination of appropriate roughness of the surface and materials with lower surface energy may be a successful way to prepare superleophobic or hydrophobic surfaces. Superleophobic surfaces were first developed through reentrant surface curvature in combination with chemical composition and the roughened texture surface by Tuteja *et.al* in 2007[9]. The samereentrant curvature structure was introduced by Cohen.*et.al* to accomplish superleophobic surfaces. Superhydrophobic hybrid film inspired by the Namib desert beetle was coated with Ag and TiO_2 nanoparticles by Chen.*et.al* [12] Moving on to an advanced level, apart fromthe work of Tuteja .*et.al*, Liu *et.al* designed doubly reentrant structures to prepare superamphiphobic coatings super repellant to completely wetting liquids [13]. In superamphiphobic and superhydrophobic surfaces, it has been noted that the droplet partially rests on air. Mechanically durable and self-healing superamphiphobic coatings use nano rod like palgorskite (PAL). Kaolin can also be used as a part of superamphiphobic coating as prepared by Qu.et.al [14]. Acid activation of clays could enhance superamphiphobicity [1]. However, the development of superamphiphobic coating with clays such as kaoline and palygorskite is in its infant state. Coalance induced drops of the coating can also be made by jumping on a superhydrophobic aluminium surface with low temperature [15].

Nowadays studies on structured hydrophobic surfaces have been focused to collect water droplets from the air. Furthermore, it is noteworthy that superamphiphobic coatings with polymer wrapped particles demonstrate excellent superamphiphobicity [2]. Jialin.*et.al* attributed that superamphiphobic surfaces are contributed by the effect of metastable ”Cassie Baxter” model originating from a rough low free energy surface [16]. An interesting way of synthesizing superamphiphobic coating has been formulated by Lujiang *et.al* which suggests that superamphiphobicity on silicon wafers can be achieved by the precise control of the surface morphology and surface chemistry [17], and the superamphiphobicity on wooden surfaces can be achieved by casting the wooden surface with fluoroalkyl silane or silica composite suspension, and there is no need for the usage of large and costly pieces of equipments. Moreover only a very low content of inorganic matter is required to achieve superamphiphobicity [18]. For generating a superhydrophobic curved surface of fibre an efficient and dynamic sliding transport mechanism is applied by meansof droplet oscillation along the fiber driven by coalescence energy release and environmental perturbation [19]. A significant finding in the usage of natural wax material that it can be used in the fabrication of superamphiphobic coating was introduced by Bayer *et.al* in his work on superhydrophobic films from self-emulsifying carban wax alcohol emulsions [20, 21]. An emulsion of molten wax, polytetrafluoroethylene particles along with thermal annealing and spray coating were done for achieving superamphiphobicity. Superhydrophobic coatings can also be prepared by spin coating [22, 23], dip coating [12, 24], plasma treatment [25], chemical etching [26,27], layer by layer assembling [28] and electro spinning [29].

2. Microscale Roughness and Superamphiphobicity:

Most of the superamphiphobic claddings are comprised of either a nanoparticle or its structure to produce surface roughness. The superamphiphobic coatings that are composed of multi-walled carbon nanotubes are meant for nano scale or micro scale coarseness. The superhydrophobic phenomenon has been observed in aligned CNT’s on account of the nano structures and the multiwalled carbon nanotubes used to create nano roughness. Researchers have found that CNT’s of one dimension can form a coralline-like structure [8], but when this CNT’s are replaced by TiO_2 and PTFE (polytetraflouroethylene) nanoparticles, the resultant coating only had a contact angle of hexadiene less than 130^0, whereas a good superamphiphobic coating has a static contact angle less than 90^0. Jie Dong *et, al* prepared clay-based super anti-wetting coatings over which clay was used as a natural nanomaterial with diverse nanostructures, and the clay was successfully modified with polymerized perflouroalkylsilane via hydraulic condensation of FDTS (Perflourodecyltricholorosilane) and TEOS (Teteraethyl orthosilicate) [1]. A combination of SiO_2 nanoparticles could create hierarchical roughness on the membrane's exterior that enables the membrane to show superamphiphobicity where robust water or oil proof and air permeable performances were also achieved [16]. Adding on to this point, when the content of SiO_2 nanoparticles in the FPU (Flourinated polyurethane) is increased was gradual increase in the wrinkles and nano protrusions between the range 100 and 250 nm were observed which resulted in the formation of hierarchical structures containing micro and nanoscale roughness [16].

2.1 Vitality of FAS:

Silane coupling agents with special characters such as hydrolyzable chemical groups and organic functional groups are used, as most silanes work by the reaction between the hydroxyl groups on the top of nanoparticles and the hydrophobic groups of the modified group in order to make it superamphiphobic [30-32]. FAS (Flouro Alkyl Silanes) play a vital role in makinga coat superamphiphobic, while nanostructures concentrate on the roughness in nanoscale upon the substrate, these flouro alkyl silanes aims on imparting phobia of the liquids. These added flouro compounds act as a low surface energy binder and its presence endows the sequel cladding with superamphiphobicity by assembling over the surface. Jie Dong *.et.al* made a superamphiphobic coating using clay as a nano material [1]. These clay particles modified successfully with polymerized perfluoroalkyl silane via hydraulic condensation of TEOS and FDTS. It is most significant to understand that fluorination carried out by the process of adding FAS improves the water repulsiveness of the coat by lowering the surface energy; contact angle increases and roll-off angle decreases [33]. The usage of Fluorinated polyurethane also helps in endowing the membrane with low surface energy [16]. The process of adding FAS17 to Cu_2O treated wood samples resulted in superhydrophobic wood surfaces [34]. In addition to this, the morphology, hydrophobicity and oleophobicity of the final covering could be tailored by varying the proportion of FAS. Both fluorinated binders and fluorinated nanomaterials are crucial for fabricating inherent superamphiphobic surfaces [8].

2.2 In Situ Synthesis:

An in situ electrode position process is used for the application of superamphiphobic cladding on electrically conductive substrates such as iron, copper, aluminium and zinc were proposed by Jiang *et.al* [35] and these coatings were found to be highly resistant to highly corrosive liquids like salt solutions, acidic and basic solutions of high pH values. An interesting fact is that electrically conductive superamphiphobic claddings can also be made by one-pot process [36].

2.3 Substrate Selection for Fabrication:

Polymers, metals, wood, aluminium sheets, glass plates, stone built cultural heritage, silicon wafers and plain weave polyester fabric were chosen as substrates and have achieved superamphiphobicity through lithography, laser ablation, anodization nanoparticle coating method or chemical etching of engineering metals in perflouro carboxylic acid [37-44]. Briefly, Xikui Wang *.et.al* have fabricated aluminum sheets because of their easy availability and low cost. For coralline structured superamphiphobic surfaces glass slides were used as substrate. The resultant surfaces often repel liquids. It is noteworthy that, the coatings are fabricated and cured under mild and ambient conditions, and do not need any special rigorous equipment and further surface modification, making them applicable to a variety of substrates in large sizes. As proof of concept, coatings on A4 paper, cotton fabric, and PET film were fabricated [8].

2.4 Nano Scale Roughness:

Superamphiphobic natural surfaces usually are composed of multiple levels of structural hierarchy, particularly micro structures covered with nano scale roughness. These surfaces support self-cleaning properties along with the reduction of damping of water and oil [45].

2.5 Course of action to attain nano Roughness:

Nanoscale roughness can be achieved in many ways. The usage of carbon nano tubes in superamphiphobic cladding is meant for nano or micro scale roughness [8]. To obtain Static Contact Angles (SCA) of about 16°, aluminium sheet is etched which on immersion with boiling water resulted in nanoscale roughness and therefore paved way to the production of superamphiphobic surfaces. Oxygen plasma etching can be used to generate nano scale roughness on fibers and to alter the porosity level [15]. Jiajie wang *.et.al* demonstrated the production of relatively uniform micro nano heirarchical structures by sanding raw wood with 240 grit sandpaper. The roughness of sanded wood decreased to be less than 100 micrometers and 5.69 micrometer [18]. The addition of polydimethylsiloxane to the carnauba wax introduced another level of uneveness on the coated exterior forming beneficiary micro or nano sized structures that result in increased water contact angle and decreased angle of the surface [20]. Jie Dong *et.al* achieved nano scale coarseness with the help of flouro POS modified Kaolonite clay nanofibres which was much worth than rectorite and illite. In addition, the cladding produced out of kaolite has many small projections which are responsible for the lower angle of surface Decane[1] . Yang si *et, al* used the blend of SiO_2 nanoparticles to create legatee roughness on the membrane surfaces [16]. All these varying nanoscale roughness indicate that they are responsible for varying SA and CA in superamphiphobicity.

3. Successful Fabrication Techniques:

Considering the coating of superamphiphobic claddings on various substrates, the two major processes include roughening the exterior especially for generating nanoscale roughness along with fluorination [46], the generation of surface roughness and surface fluorination can occur in the same step which is denoted as one pot or in situ fabrication techniques.

3.1 Spray Casting:

For achieving superamphiphobic structures with coralline structure, the coating was obtained by *spray casting* the nanocomposites onto the clean glass slides. The distance between the airbrush and the glass slide was approximately found to be 15cm and the working pressure was 0.2MPa [8]. The same process was carried out by Jie Dong *.et.al* and Xiaolong Wang *et.al* [1,8].

3.2 Spray Coating:

Ilker Torun *et.al* used natural wax for the preparation of amphiphobic claddings on[20] glass monolayer of size 2×2 cm^2 were washed using acetone, ethanol and distilled water, and then made moistureless using nitrogen flow. The substrate was then subjected to a UV ozone cleaning process for 30 minutes. With a nozzle of inner diameter 0.35mm, pressure of 2 Bar, working distance of 15cm, and coating angle 75°. This results in a coat layer of thickness 14micrometer.

3.3 Oxygen Plasma Etching:

Etching with oxygen plasma is a fabrication technique that generates nano sized uneveness.The process is carried out in a way that thin substrates like paper are placed in a 2.5-inch parallel plate in a plasma reactor and etched for times between 15 and 60 min. After this process, the reactor was evacuated to 0.01 Torr, oxygen was introduced into the reactor at 20 standard cubic centimeters per min along with equilibrium pressure of 0.5 Torr is established. The process of etching was conducted at 110^0C using a power of 120W. The radio frequency power was provided at a frequency of 13.56MHz.

3.4 Sanding of Wood Substrate:

Jiajie Wang *et.al* used raw wood as a substrate. This wood was fabricated by sanding with 240 grit sandpaper, hence forming a cassie baxter state in which air in the uniform pores can reduce contact areas between droplets of water and the surface [48] to modify the natural hierarchical structure of the wood and further it is coated with KH1322 and silica.

3.5 Chemical Etching:

Common engineering metals like zinc, aluminium, iron, nickel, and their alloys can be chemically etched by taking advantage of an electrochemical reaction in perflourocarboxylic acid solutions, through control over the chain length, the concentration of perflourocarboxylic acid established rough superamphiphobic structures[37].

3.6 Durability of Superamphiphobic Claddings:

Surface durability of a superamphiphobically coated exterior is an extremely important characteristic that determines the ability to use non-wetting surfaces in commercial applications. Wetting properties and the resilience of a exterior with amphiphobic coating are the main evaluation criteria for the wetting properties. Despite its significance in nearly all potential applications Kim *et.al* and Paven and group have investigated the mechanical robustness of superamphiphobic coatings [49, 50]. The sturdiness was tested by exposing the fabric to elevated aerodynamic shear and multiple flows. To determine the durability contact angle of water and roll-off angles are presented for both the airfoil configuration and the hydrophobic fabrics in the flat plate configuration. Polyester fabrics even under icing conditions maintained favorable wetting properties after being exposed to a range of aerodynamic and multiple flow conditions like the icing of aircraft. When damaged slightly, they retained a high contact angle and much of the changed, but their chemistry and micro structure remained intact, but when exposed to external environments like on a car, the conditions are less controlled. Also a disadvantage is that chemical degradation can occur on the organic fluorine groups that occur after prolonged exposure to UV radiations.

Superamphiphobic biomimetic anti wetting coatings based on nanoclay were found to have excellent mechanical sturdiness against intense water jetting, high chemical resilience under UV irradiation and on immersion in various corrosive fluids, and on elevated thermal solidity up to 350^{o}C. Preparation of extremely thin coating allowed the investigation of changes in the wetting properties, neither the durability, nor the adhesion of the substrate degraded after sand impingement test, this indicated that the coating can repel liquid in an array of applications. Breathable membranes were found to exhibit sturdy durability even when loaded with 1.5kg water or oil at the same time while maintaining a high air permeability of 2Lm^{-1}. Wood when coated with superamphiphobic coating was found to be satisfactorily resistant to abrasions and can self-heat at normal temperature upon damage. On the depletion of the healing agent, the surface was able to restore it by casting FAS\ silica composite. By increasing the water resistance of wood, the service life of wood-based materials could be increased. The superamphiphobic coat from carnauba wax exhibited outstanding resilience to water influence. The superhydrophobic porous polymeric surface exhibit good chemical and thermalstability.

4. Dynamic Applications:

Water, a keyword of the century can be saved, harvested, and can be collected without being polluted by the help of superamphiphobic coverings, especially in regions of semi-arid deserts and inland areas for overcoming water shortage problems. Furthermore, fog or water collection, desalination, anti-fogging, and heat delegate find the applications of superamphiphobicity to be useful. The SAPC’s prepared with the help of acid-activated clays spot application in anti-adhesion and anti-climbing of liquids of minimal surface tension, coralline structured superhydrophobicity and superleophobicity have become very desirable for its dynamic requisition in green construction, liquid repellent material, self-cleaning products and microfluidic systems. Xiaolong and his group have experimented that the thin coating on the A4 paper can be blown away easily and Ch_2I_2 droplets can move freely on the coating sprayed on cotton fabric. This indicated that the cladding is uniformly superamphiphobic with very low adhesion to water and oil giving them extensive application in areas of liquid transport, self-cleaning, and anti-contamination. Adding on to the work of Wang *et.al*, Xiochen Ma too found that the superamphiphobic coatings on the aluminium surface with random micro nanocomposite structures with an integrated device called TENG (Tribol Electric Nano Generators) found their significance in dew collection in harvesting water and relieving water shortages in arid regions [15].

Prevention of icing and relieving the surface of ice contamination can be overcome by coating with a superamphiphobic coating. An easy to clean superamphiphobic coating removes the insect contamination and frost without the use of a hand tool as the flexible nature of the fabric helps to break the ice apart. A staggering number of hydrophobic technologies and processes have been published in recent years [51, 52]. Yang Si *et.al* synthesised FPU-18 SNP-1 membranes that possessed excellent water or oil-proof and breathable performances, which could be applied as promising mate-rials for a wide range of potential applications in protective clothing, bioseparation, water purification, tissue engineering, and microfluidic systems. Lu Jiang *et.al* concluded that the superamphiphobic coatings found a subtle effect in the archiving of paper files, disposable wearable garments, and non-greasy food and liquid packaging with mechanically stable surfaces by using a simple and efficient production cycle. Construction of superhydrophobic surfaces by coating fluoroalkyl silane or silica composite exhibited satisfactory resistance to abrasion and can self-heal at room temperature upon damage. When used for the protection of wood, these superhydrophobic surfaces greatly improved both mildew inhibition and water resistance of wood, thereby prolonging the service life of wood-based materials. Their excellent performance, facile and environmentally friendly fabrication process, and low cost make this method highly suitable for the protection of various wood-based materials[18].

Fotios.G.Adamopoulos *.et.al* found that the application of superamphiphobic coatings with TEOS-based materials was able to protect the marble surfaces without using engineering nanoparticles whereas the deposition method does affect the wetting properties[38] . The applications of carnauba wax with PDMS coatings exhibited superb superhydrophobic and self-cleaning behaviour. These caotings can be used to coat paper and other materials like a household sponge which is used in the cleaning of vessels, that did not show any discernible wetting even when placed on a tissue paper. This oleophilic property of the composite carnauba wax and PDMS coated sponge can be used widely in cleaning up oil spills [53,54] . Apart from these applications superamphiphobic surfaces exhibit great potential in a variety of fields including breathable protective wear[46] , enhanced solvent resistance, chemical shielding, drag reduction, patterned super functional surfaces, smart devices, anti reflection and oil capture [55-58]. .

5. Conclusion

This review summarizes most aspects of a successful superamphiphobic coating. The fabrication techniques along with, the advantages were studied and discussed in detail and was demonstrated for each process in detail. The following processes have been discussed, in situ synthesis, spray casting, spray coating, oxygen plasma etching, sanding of wood, and chemical etching. Along with fabrication techniques, the properties and durability with application were also discussed. Taking a quick view on the best application techniques, in situ synthesis and spray coating are noteworthy. They are of a good yield of the desired product. In situ synthesis is a single pot synthesis in which the electro deposition process is involved. The coatings produced by this process were found to be highly resistant to corrosive liquids with very low or high pH values. Spray coating is a widely used technique with a high success rate as the coating layer with a thickness of 14 micrometers could be obtained.

A considerable number of scientists have contributed their valuable efforts in the field of superamphiphobicity which is of high impact on the collection of water, self-cleaning, anti- wetting, anti-fowling, oleophobicity and hydrophobicity. The stunning performances of the superamphiphobic coatings make them vital in the upcoming years. Low cost of materials and easy production techniques make them highly demanded in the field of antiwettability. Surfaces with controllable superhydrophobicity and superleophobicity may become one of the focus studies in future research. The future of the superamphiphobic surfaces will be witnessed as many scientists and engineers contribute to the understanding and the design of such studies.

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