CHAPTER 3

Methods and fabrication techniques of superhydrophobic surfaces

Aditya Kumar[a], Debasis Nanda[b]
[a]Department of Chemical Engineering, Indian Institute of Technology (Indian School of Mines), Dhanbad, India
[b]Department of Chemical Engineering, National Institute of Technology, Rourkela, India

1. Introduction

Surfaces with high water contact angle (>150 degrees), low sliding angle, antisticking, anticontamination, and self-cleaning effect are called superhydrophobic. These properties are attractive for many industrial and biological applications such as antibiofouling paints for boats, antisticking of snow for antennas and windows, self-cleaning windshields for automobiles, microfluidics, lab-on-a-chip devices, metal refining, stain-resistant textiles, antisoiling architectural coatings, and dust-free coatings on building glasses [1–6]. In nature, many kinds of special surfaces such as lotus leaves, rice leaves, butterfly wings, mosquito eyes, moth eyes, cicada wings, red rose petals, gecko feet, desert beetle, spider silks, and fish scales exhibit excellent hydrophobicity and/or superhydrophobicity [7–12]. These natural structures suggest new idea for designing the artificial superhydrophobic structures.

There are mainly two approaches of producing superhydrophobicity: creating hierarchical structures (micro- and nanostructures) on hydrophobic substrates or chemically modifying a hierarchical structured surface with a low surface energy material [13–20]. The various methods synthesis of superhydrophobic/oleophobic surfaces have been reported in literature such as electrochemical deposition [21], phase separation [22], emulsion [23], plasma method [24], template method [25,26], electrospinning [27], solution immersion [28], chemical vapor deposition (CVD) [29], wet chemical reaction [30], crystallization control [31], sol-gel processing [32–35], lithography [36], and others [37–39]. Some of these are simple and inexpensive; however, some of these involve multistep procedures and harsh conditions or require specialized reagents and equipment, which leads to increase the cost of coating.

Isotropic, high roughness, transparent superhydrophobic surfaces can be created using plasma etching; however, it requires costly precursor leading to increasing cost of coating. Chemical etching process creates hierarchical structures. Although it is cheap, simple, and facile method, but there are complication of mask selection and anisotropic etching. X-ray or atomic force microscopy (AFM) lithography creates regular patterns, but it

Superhydrophobic Polymer Coatings
https://doi.org/10.1016/B978-0-12-816671-0.00004-7

requires very costly equipment. Photolithography is also costly as well as slow process for producing high roughness and large area of periodic micro/nano patterns. Electron beam lithography can create accurate and excellent nanostructured superhydrophobic coatings, but it is having issues of charging, shot noise, and interaction between parallel electrons. Nanoimprinting process creates hierarchical structure superhydrophobic surfaces and is cheap and efficient process; however, this is having issue of overlay, bubble defects, template patterning, and template wear. Self-assembly is a facile, cheap, and time-saving method, but it requires a suitable precursor and defects due to weak intermolecular interaction. Electrochemical method is efficient, fast, facile, and low cost, but it is not environmental friendly. Among all synthesis techniques, dip coating, spray, spin, and sol-gel methods are cheap, fast, and easy to produce accurate and homogeneous superhydrophobic surfaces.

Since several years, the endless efforts have been carried out to develop the synthesis techniques to prepare superhydrophobic/oleophobic surfaces for industrial scale which are economical, easy to produce, environmental safe, high efficient, well adhesive, compatible, and high durability; but most of them are restricted to only fundamental research in laboratory and there is still much work required to be done for superhydrophobic/oleophobic surfaces preparation on commercial scale.

2. Theoretical background

Wetting of the surface takes place when water droplets spread on the surface and spreading is generally due to the presence of high-energy molecules on the surface which has a high affinity toward water. Static contact angle of the water droplet for these surfaces is found to be low. On the other hand, to repel water droplets from the nonwetting surfaces, static contact angle of water droplets need to be high. Increase in the contact angle of water makes the droplet spherical in shape which makes the minimum contact of droplet on the surface.

Static contact angle of water on a surface is determined by Young's equation (Eq. 1) on the rested droplet on the surface as shown in Fig. 1.

$$\gamma(\mathrm{sv}) - \gamma(\mathrm{sl}) - \gamma(\mathrm{lv}) \cos\theta = 0 \tag{1}$$

where θ is the contact angle, γ(sv) the solid-vapor interfacial energy, γ(sl) the solid-liquid interfacial energy, and γ(lv) the liquid-vapor interfacial energy.

Based on the contact angle, wettability of the surface is also divided into four types, that is, superhydrophilic ($\theta \sim 0$ degrees, complete wetting of the surface), hydrophilic ($\theta < 90$ degrees, partial wetting of the surface), hydrophobic ($\theta > 90$ degrees but < 150 degrees, partial nonwetting of the surface), and superhydrophobic ($\theta > 150$ degrees, complete nonwetting of the surface).

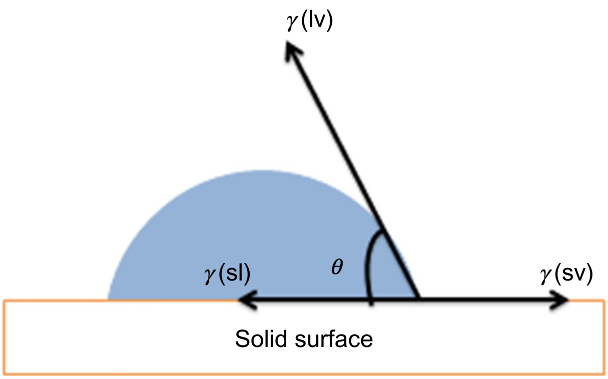

Fig. 1 Schematic diagram of contact angle measurement by Young's Experiment.

Another factor for surface to be self-cleaned is sliding angle or contact angle hysteresis which is shown in Fig. 2. It is measured by the difference between the advancing contact angle (θ_a) and the receding contact angle (θ_r) formed when the sample is tilted and liquid droplet starts to roll down due to the gravitational force. For self-cleaning application of superhydrophobic surface, the sliding angle of the sample must be <10 degrees.

Roughness plays an important role in generating superhydrophobic surfaces. Water droplet behavior changes according to the roughness. There are mainly two proposed models based on the roughness for superhydrophobic surface and these are:

2.1 Wenzel state

Wenzel state was proposed by Robert N. Wenzel [40]. It defines that the superwetting surface with roughness is a homogenous surface with no air pockets between the grooves as shown in Fig. 3.

When a droplet is placed on the surface, part of it penetrates into the grooves and subsequently it reduces the static contact angle and increases the sliding angle.

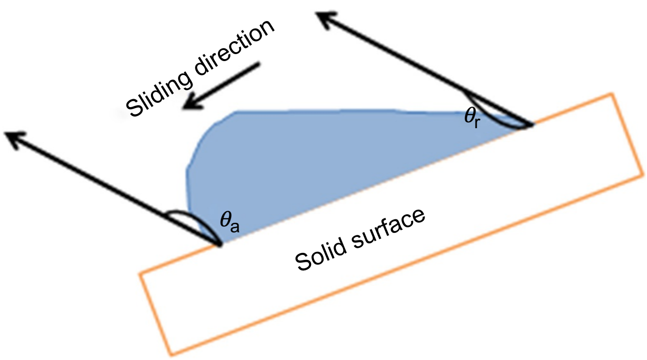

Fig. 2 Schematic diagram of contact angle hysteresis.

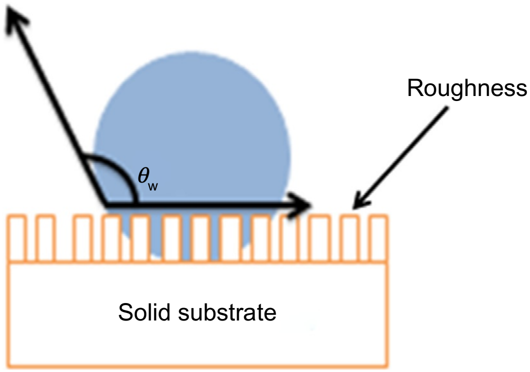

Fig. 3 Schematic diagram of Wenzel state on superwetting surface.

Increase in the sliding angle is due to the locking of droplet in between the grooves which is called as pinning. Wenzel proposed an equation which is given by

$$\cos \theta_w = r \cos \theta \tag{2}$$

where θ_w is apparent contact angle which corresponds to the stable equilibrium state, r is roughness factor, and θ is Young's contact angle. Roughness factor is defined as ratio of true area and apparent area of the solid surface. Value of roughness factor is 1 and >1 for smooth and rough surface, respectively. According to the Wenzel theory, with increase in roughness wettability increases for hydrophilic surface. Whereas the adverse condition of wettability takes place for hydrophobic surface.

2.2 Cassie-Baxter state

This model was proposed by Cassie and Baxter [41]. It defines that rough surface is heterogeneous in nature with air pockets present in between the grooves of the roughness. Droplet remains on the surface and does not penetrate through it as shown in Fig. 4.

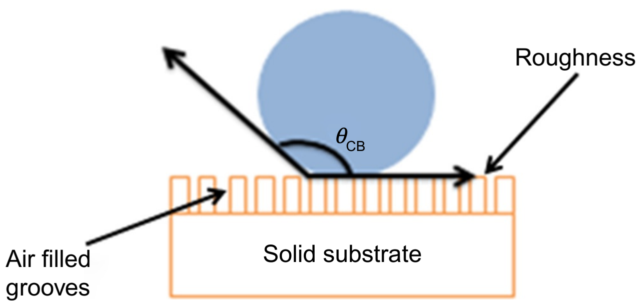

Fig. 4 Schematic diagram of Cassie Baxter state on superwetting surface.

In this model, the sliding angle or contact angle hysteresis is low compared to the Wenzel model. The Cassie-Baxter equation is given by

$$\cos\theta_{CB} = f_1 \cos\theta_1 + f_2 \cos\theta_2 \quad (3)$$

where θ_{CB} is the Cassie-Baxter contact angle, f_1 and f_2 are the surface fraction of phase 1 and phase 2, and θ_1 and θ_2 are the contact angle on phase 1 and phase 2. For the air-liquid surface, Eq. (3) can be further reduced to

$$\cos\theta_{CB} = f \cos\theta + f - 1 \quad (4)$$

where f is the solid fraction, that is, fraction of solid surface is wetted by the liquid.

Transition of the state from Cassie-Baxter state to Wenzel state can take place by applying pressure on droplet [42], varying the droplet size [43], and impact of droplet or by vibration [44,45].

3. Synthesis techniques

There are two main approaches for creating superhydrophobic surfaces: creating micro/nano-hierarchical structures on hydrophobic substrates and chemically modifying a hierarchical structured surface with a low surface energy material such as fatty acid, polymers, hydrocarbons, and fluorocarbons. The various methods of synthesis of these surfaces have been reported in literature such as electrochemical deposition, phase separation, emulsion, electrospinning, immersion, CVD, wet chemical reaction, lithography, and others. This chapter provides the overview of the recent progress in the synthesis and difficulties arise during the implementation of superhydrophobic surfaces.

3.1 Dip coating technique

Dip coating technique is a well-suitable process for the production of nanometric thick coatings. It is a continuous process in which the substrate is immersed into a solution of the material to be deposited at a constant immersion rate. After immersing of substrate in solution for a period, it starts to be pulled up. The film is deposited on the substrate while is pulled up. The withdrawal or pulling speed controls the thickness of the film. High speed produces a thin film. The excess of solution is drained from the surface while withdrawing. The solvent present in solution is evaporated, resulting a coating on the surface. It has several advantages such as simultaneous coating of top and bottom part of substrate, no wastage of material, suitable for all kind of materials, high output, uniform, highly durable, compact, stable coatings, and easily repairable. However, in this process, all components used in coating have to be submersible.

Using the dip coating technique, several works on superhydrophobicity have been published. For example, Zhang et al. [46] carried out a simple dipping process for the preparation of superhydrophobic coatings based on titanium dioxide nanowires dispersed in tetrahydrofuran (THF) followed by the addition of polydimethylsiloxane (PDMS). Coating showed the water contact angle of 158 ± 2 degrees. After UV irradiation water contact angle reduced to 25 degrees. Coating had self-cleaning property.

Cui et al. [47] constructed a three-step procedure for fabrication of superhydrophobic epoxy paints through sandblasting and anchoring of SiO_2 nanoparticles. To enhance hydrophobicity, it was dip coated with modified epoxy adhesive. The apparent contact angles were found as high up to 167.8 ± 1.6 degrees. These superhydrophobic surfaces showed high durability and stability against scouring tests, neutral and basic aqueous solutions, organic solvents such as toluene and ethanol.

Klien et al. [48] fabricated a superhydrophobic surface on a polycrystalline alumina substrate by dip coating technique with a dilute suspension which was formed by dispersing nano-silica spheres. After a low-temperature heat treatment, the particles adhered to the surface. The surface was made hydrophobic by a reaction with a solution containing fluoroalkyltrichlorosilane which resulted in hydrophobicity increase due to decreasing area fraction of spheres.

Cengiz et al. [49] produced superhydrophobic and oleophobic rough copolymer surfaces by phase separation method using styrene-perfluoromethacrylate random copolymers which were dip coated on glass slides with THF and methyl ethyl ketone mixture containing methanol as nonsolvent. An increment of 146–160 degrees for water contact angle and 65–90 degrees for hexadecane contact angle was obtained.

Mahadik et al. [50] developed a simple and inexpensive method to fabricate superhydrophobic surfaces by preparing superhydrophobic silica coatings using organic-inorganic silica precursor methyltrimethoxysilane (MTMS) on quartz substrate by dip coating method. The water contact angle was achieved as 168 ± 2 degrees and water sliding angle as 3 ± 1 degrees. This coating surface showed properties of water repellency and superoleophilic nature along with the durability, thermal stability, and optical transparent nature.

Ramezani et al. [51] fabricated transparent superhydrophobic silica films by dip coating process on a glass substrate. These films have properties like high optical transmission and thermal stability. The water repellency of the silica films was controlled by a surface-modifying agent isooctyltrimethoxysilane (iso-OTMS). The maximum contact angle was achieved as 160 degrees. By using dip coating technique, Gao and He [52] developed broadband antireflective superhydrophobic coatings based on three types of sol: (1) silica sol obtained by hydrolysis of tetraethyl orthosilicate (TEOS) under acidic condition, (2) silica nanoparticle suspension prepared by Stober method, and (3) mesoporous silica nanoparticle suspension followed by CVD of 1*H*,1*H*,2*H*,2*H*-perfluoro octyltriethoxysilane. The maximum transmittance of coating achieved was 95.3% at a wavelength of 630 nm with a water contact angle of 153 degrees and sliding angle of <5 degrees. These antireflective superhydrophobic coatings have promising applications in solar cells optical detection, sensors, etc.

Liu et al. [53] fabricated a compact TiO_2 coatings on anodized aluminum surface by vacuum dip coating technique. This coating prevents aluminum corrosion in seawater.

Rao et al. [54] used dip coating technique to coat water-repellent porous silica films on glass substrate. A maximum static contact angle of 164 degrees and minimum sliding angle of 4 degrees was achieved. These films have self-cleaning and anticorrosive applications.

Nanda et al. [55] dip coated aluminum surface to make the surface superliquiphobic (both superhydrophobic and superoleophobic) in nature with self-cleaning and antifogging properties. The coated sample was stable to thermal, mechanical, and chemical test. Superliquiphobic surface was able to repel water, ethylene glycol, glycerol, and hexadecane from its surface and showed contact angle of 168.0 ± 2.7 degrees, 165.0 ± 4.0 degrees, 166.0 ± 3.5 degrees, and 155.0 ± 4.1 degrees with sliding angle of $<3.0 \pm 0.5$ degrees, $<4.0 \pm 0.5$ degrees, $<4.2 \pm 0.5$ degrees, and 6.2 ± 0.5 degrees, respectively.

Sun et al. [56] fabricated superhydrophobic surfaces on zinc substrate by electrochemical processing using a mixed electrolyte composed of $NaNO_3$ and NaCl followed by dip coating process with fluoroalkylsilane ethanol solution. The maximum water contact angle achieved was 165.3 degrees and tilting angle of 2 degrees.

3.2 Spin coating technique

Spin coating technique is used for making a thin coating on relatively flat substrates. The solution of material to be coated is deposited onto the substrate which is spun off at a high velocity in a range of 1000–8000 rpm and leaving a uniform layer. The angular speed, the solution viscosity, and the spinning time determine the ultimate thickness of the deposited film [57]. Thickness of film can be changed by changing spin speed or switching to a different photoresist. It is an excellent technique on laboratory scale. Despite of all advantage, it has demerit of incapable for large substrate, lack of material efficiency, and cost of disposal.

By employing spin coating technique, several works on superhydrophobicity have been published. For example, Soz et al. [58] carried out multistep spin coating of dispersed hydrophobic fumed silica on polymer-coated glass surface. Prior to coating, two different surfaces were developed on the glass surface by spin coating polymer films [hydrophobic segmented silicone urea copolymer and hydrophilic poly(methyl methacrylate) (PMMA), respectively]. The prepared sample exhibited contact angle >150 degrees with an average roughness of 125–150 nm.

Zhang et al. [59] prepared a MgAl-layered double hydroxide (LDH) film by spin coating a nanodispersed MgAl-LDH sol on an AZ31 magnesium alloy substrate. The corrosion resistance offered by the LDH films increases with the thickness of the film. These LDH films were also environment friendly corrosion-resistant coatings.

Eskandari et al. [60] used copper (II) acetate as a starting material for the preparation of cuprous oxide thin films and treating them in N_2 atmosphere at low temperature through two-step sol-gel spin coating method. The contact angle achieved here is 45 degrees which results in hydrophilic surface and the surface can be used in photoelectrochemical application such as water splitting.

Zhang et al. [61] fabricated photoresponsive superhydrophobic surfaces by immobilizing fluorinated azobenzene derivatives onto silica surfaces which was prepared by spin coating silica particles on silicon wafers followed by modification with polydopamine. The water contact angle achieved was more than 150 degrees and the contact angle hysteresis was <10 degrees.

Xu et al. [62] fabricated transparent and robust superhydrophobic surfaces by spin coating of fluorosilane-modified silica nanoparticles on surfaces such as Si wafers, glass substrate, PMMA, and polyester fabric. In this method, pre- and posttreatment of the substrate was not required. The advancing water contact angle achieved was more than 150 degrees and water droplet roll-off angle was <5 degrees.

He and Wang [63] fabricated superhydrophobic ZnO nanorods on zinc foil substrate by electrochemical deposition. After being spin coated by perfluoroalkyl methacrylic copolymer (Zonyl 8607) over the ZnO surface, the maximum contact angle achieved was 167 degrees. It finds application as anticontamination, antifouling, and self-cleaning films.

3.3 Spray coating technique

In this technique, solution of materials to be coated is sprayed on the substrate by means of spray gun. The coating precursor is generally heated-melted by electrical or chemical means. This process is having several advantages such as simple, high availability, possibility of automation, quick, cost effective, repairable, and nontoxic. This technique can also be applied on substrates like plastics, metals, and fabrics. This coating method also finds applications in self-cleaning wind shields in automobiles and anticorrosive applications. Besides all the merits, it has also some limitations such as wastage of the material compared to other processes, high consumption of material, over spray, difficult to produce thick coatings, low degree of adhesion on small substrate, and extremely difficult for the substrate with small curvature.

Using this technique, several works have been published. For examples, Kim and Cho [64] used airbrush of 400 μm diameter nozzle for spray coating a sol-gel of polystyrene (PS) and multiwalled carbon nanotubes (MWCNTs) on cover glass. The prepared sample showed mechanically and aging stable superhydrophobic property with water contact angle of 163.8 ± 2.5 degrees and water sliding angle 5.0 ± 0.9 degrees.

Zhang et al. [65] synthesized superhydrophobic aluminum by single-step spray coating with sol-gel of methylsilicate functionalized hydrophobic SiO_2 nanoparticles and glass resin on chemically etched aluminum surface. The developed sample was mechanically stable with regenerable property and has a static water contact angle of 155 degrees and a roll of angle of 4 degrees.

Cui et al. [66] prepared a micelle solution of PS and comb-structured fluorinated main chain with narrowly dispersed grafted chain. This micelle solution was then spray coated on aluminum oxide particles sandblasted glass surface to change its wettability to superhydrophobic. The sample exhibited maximum contact angle of 160 degrees and the sliding angle <6 degrees.

Ma et al. [67] created easily restorable superhydrophobic coating on cellulose substrates like leather, cotton fabrics, and filter papers. First, the polyacrylate emulsion was spray coated on the surface followed by spray coating hydrophobic silica nanoparticles. Superhydrophobicity was achieved with static contact angle of 170.3 degrees and sliding angle of 2 degrees after having eight layers of HN-SiO_2 spray coated on it.

Latthe and Rao [68] used single-step spray coating method to achieve superhydrophobic coating on glass surface by spraying sol-gel of MTMS and derived SiO_2 microparticles. The coating increased the contact angle of water to 162 ± 2 degrees and roll-off angle of 6 ± 1 degrees.

Tarwal et al. [69] created superhydrophobic surface on glass surface using spray pyrolysis technique (SPT). Seed-assisted growth of polycrystalline thin-film ZnO was prepared on glass surface which showed a maximum contact angle of 165 degrees which assured its applications in different fields like smart windows, biochips, environmental cleanups, microfluid devices, etc.

Ovaskainen et al. [70] used spray coating of rapid expansion of a supercritical solution (RESS) technique to make the surface of silica wafers superhydrophobic. Solution of poly (ε-caprolactone) (PCL) and a statistical copolymer of vinyl acetate and vinyl pivalate [P(VAc-VPi)] was coated in the presence of acetone as cosolvent which increased the static contact angle ranging from 120 to 155 degrees.

Xu et al. [71] fabricated chemically inert and anticorrosive superhydrophobic coating on copper mesh using single-step spray coating technique. The sample was prepared by the reaction of metals and alkanethiols which was formed by solution of silver nitrate in ethanol solution and *n*-octadecanethiol. The sample showed a static contact angle of above 158 degrees for different pore size mesh.

3.4 Electrochemical deposition technique

The principle of electrochemical deposition is inducing chemical reactions in an aqueous electrolyte solution with the help of applied voltage. Getting material into arbitrary three-dimensional (3D) geometry is a great strength of this process. It is also a low-energy process and therefore, uniquely suited for dealing with modification of soft matters. It also offers unique spatial selectivity and is flexible and cheap process [72]. It is well suited of nano-, bio-, and microtechnologies. It can be used to grow functional material through complex 3D masks. It can be performed near room temperature from water-based electrolytes. It can be scaled down to the deposition of few atoms or up to large dimensions. This method is time saving, environment friendly. The main limitation of electrochemical deposition is in size and strength. It is only suitable for selected size and poor strength of structures. Moreover, it is required high temperature during deposition and has less control in growth.

This technique has potential to contribute for fabrication of superhydrophobic metal coatings industrially. For example, Liu et al. [73] synthesized controlled adhesion superhydrophobic coating on copper surface by one-step electrodeposition method. The adhesion force was controlled based on the reaction time. The copper surface was immersed in an electrolyte solution of cerium chloride and myristic acid in ethanol which increased the water contact angle to maximum of 161.7 degrees after 30 min of electrodeposition with low adhesion. It is observed that superhydrophobic property was achieved after 10 min of reaction time with high adhesion. Further increase in time the adhesion force reduces and had a low adhesion at 30 min of reaction time. The prepared sample was stable to different pH and also showed anticorrosive property.

Cao et al. [74] prepared superhydrophobic Bi/Bi_2O_3 surface by two facile single-step methods, that is, displacement reaction and electrodeposition. A layer of Bi_2O_3 was developed by the deposited Bi by surface passivation that changed the surface morphology to hierarchical porous dendritic structures that increased the water contact angle to 164 degrees.

Zhao et al. [75] changed the wettability of stainless steel surface to superhydrophobic by electrochemical deposition. First, microstructures were created by polishing with abrasive paper and then the roughed surface was electrodeposited by $Cu(CH_3(CH_2)_{12}COO)_2$ for 3 h that increased the water contact angle to 154.5 degrees.

Zhang et al. [76] changed the layer-by-layer (LBL) coated polyelectrolyte surface of indium tin oxide (ITO) to superhydrophobic by electrodeposition method with gold clusters. The prepared sample had a water contact angle of 156 degrees after 1000 s of electrodeposition followed by immersing overnight with *n*-dodecanethiol. The contact angle further increased to 173 degrees after 40 min exposure to ambient temperature.

Li et al. [77] developed a thin film of conductive hydrophobic zinc oxide layer on ITO glass substrate. The zinc oxide layer was deposited by cathodic electrochemical deposition. The wettability was then further decreased by modifying the surface with hydrolyzed (heptadecafluorodecyl)trimethoxysilane that increased the contact angle of water to 152 ± 2 degrees. The prepared superhydrophobic conductive thin films have an application in developing microfluidic devices.

Gnedenkov et al. [78] synthesized anticorrosive titanium, low-carbon steel, and magnesium alloy by deposition of silica nanoparticles dispersions on pretreated plasma electrolytic oxidation (PEO) metal surfaces. The roughed surface was further treated with

N,*N*,*N*-trimethyl-1-{3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-oxy]-propyl}-silane that increased the contact angle of water higher than 160 degrees.

Wang et al. [79] prepared biomimetric hierarchy structure on aluminum surface by three different steps. First, anodized porous alumina (APA) fabrication technique was used to form a template. These templates were electrodeposited by nickel and copper to form nanometer pillars between the pores of the aminopropyltriethoxysilane (APS) developed alumina surface. The roughed surface was then treated with fluoroalkylsilane that increased the contact angle of water to 152 degrees, tilt angle of 6 and 157 degrees, and tilt angle of 3 degrees for nickel and copper deposited nanopillars, respectively.

Mahajan et al. [80] developed superhydrophobic coating with static contact angle of 177 degrees on the surface of copper foil. Porous copper were deposited on the surface by electrodeposited galvanostatically via a hydrogen bubble templating method in the presence of CuTCNQ and $CuTCNQF_4$.

He and Wang [63] reduced the wettability of the zinc surface as the contact angle increased to 167 degrees by electrochemical deposition method. ZnO nanorods were grown on the surface of ZnO film by electrodeposition followed by spin coating with perfluoroalkyl methacrylic copolymer to achieve superhydrophobicity. The prepared samples have a promising application in the field of anticontamination, antifouling, and self-cleaning films.

Sun et al. [56] changed the surface of zinc surface to superhydrophobic by electrochemical processing in the presence of mixture of $NaNO_3$ and NaCl as electrolyte. The roughed surface was then dip coated in fluoroalkylsilane ethanol solution that increased the contact angle of water to 165.3 degrees and sliding angle of 2 degrees.

Huang et al. [81] electrodeposited copper on the surface of aluminum to create the desired roughness. The roughed surface was again electrochemically modified by stearic acid to increase the contact angle to 157 degrees.

Han et al. [82] developed superhydrophobic magnesium surface by electrodepositing of nickel on the surface followed by reducing the surface energy by stearic acid to achieve a contact angle 144.5 degrees.

3.5 Chemical etching process

Chemical etching is a process in which the surface elements are made to react by wet method, that is, by using highly acidic or basic solutions. It is required simple equipment with no capital investment. It provides high etching rate and high selectivity; therefore, it is fast process. The technique used is ecofriendly and also corrosion resistant. Along with many advantages, it has some demerits. It leads the contamination of the substrates. It requires high amount of etchant chemicals as they have to be consistently replaced in order to keep the same initial etching rate. It has poor process control.

Many studies have been reported in synthesis of superhydrophobic surfaces on different substrates using chemical etching method. For instance, Qian and Shen [83] chemically etched the surface of aluminum, copper, and zinc with Beck's dislocation etchant, Livingston's dislocation etchant and HCl solution, respectively. The etched surfaces were then immersed in the solution tridecafluoroctyltriethoxysilane to change the surfaces top superhydrophobic. Static water contact angle of 156, 153, and 155 degrees were achieved for aluminum, copper, and zinc after 15 s, 24 h, and 90 s of etching, respectively followed by fluoroalkyl treatment.

Quan et al. [84] synthesized antiicing coating on the surface of copper and aluminum surfaces. The surfaces were roughened by chemical etching with HCl solution followed by mixture of NaOH and $(NH_4)_2S_2O_8$ for copper surface. Similarly, aluminum surface was chemically etched by solution of equi-volume of oxalic acid and hydrochloric acid. The etched surfaces were treated with stearic acid to achieve a contact angle of 158.3 degrees and 158.6 degrees for copper and aluminum, respectively.

Qi et al. [85] prepared self-cleaning, antireflective coating on silicon wafer by chemically etching the surface with KOH and silver catalytic etching. The etching produced a hierarchical structures of pyramidal type which when treated with heptadecafluoro-1,1,2,2-tetrahydrodecyl triethoxysilane to increase the contact angle to 169 degrees and sliding angle <3 degrees.

Shi-heng et al. [86] developed superhydrophobic aluminum surface with contact angle of 151.3 degrees by chemically etching the surface by NaOH in ultrasonic bath followed by modifying the surface with 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane.

Xie and Li [87] also fabricated superhydrophobic coating on surface of aluminum plate by chemically etching the surface with boiling aqueous solution of NaOH and then modifying the etched surface with lauric acid. The superhydrophobic aluminum surface exhibited a contact angle of >150 degrees.

Hao et al. [88] changed the surface of zinc into superhydrophobic and oleophobic where the water contact angle and peanut oil contact angle were measured to be 151.85 degrees and 145.62 degrees, respectively. The dual property on zinc surface was achieved by chemical etching with HCl followed by hydrothermal treatment with ammonium hydroxide. The etched surface was then modified by perfluorooctanoic acid to make the surface repel both water and oil.

Liao et al. [89] created roughness of micro/nano binary structures by chemically etching the aluminum surface first by $CuCl_2$ to achieve microstructures then by HCl to form nanostructures. These roughed surfaces were then treated with hexadecyltrimethoxy silane to achieve a contact angle of 161.9 ± 0.5 degrees. The prepared samples showed antiicing property and were stable to high temperature, exposure to sea water and sand abrasion test.

Liu et al. [90] created the roughness on aluminum surface by chemically etching the surface with hydrochloric acid. The etched surface was coated with polypropylene and

PS and polypropylene grafting maleic anhydride to make the surface superhydrophobic with contact angle of 157 degrees and 159 degrees, respectively.

Shen et al. [91] developed superhydrophobic coating on Ti_6Al_4V alloy surface. Surface was first sandblasted to create micro-roughness on which nanostructures were created. Different nanostructures such as nanowire by hydrothermal method, nanotube by anodic oxidation and nanomesh by two-step chemical reaction were developed. These surfaces were then modified with FAS-17 that increased the contact angle to 161 degrees and tilting angle of 6 degrees.

Xu et al. [92] achieved a contact angle of 151 degrees on the surface of copper foil by wet chemical etching method. The surface of copper foil was chemically etched with sodium hydroxide and sodium persulfate. Further, a thin film of Au was sputtered on this etched surface followed by surface modification by *n*-dodecanethiol solution to make the surface superhydrophobic.

Li et al. [93] achieved superhydrophobic property with low friction coefficient and anticorrosive property on copper surface. The superhydrophobic coating on copper surface was carried out by two-step immersion method. The surface roughness were created by acid etching in solution of $(NH_4)_2S_2O_8$ and HCl and then immersion in silver nitrate solution (replacement reaction). The roughed surface was then modified with stearic acid to increase the water contact angle to 160.5 degrees.

Lee et al. [94] developed superhydrophobic silicon surface with contact angle $\sim$180 degrees. The silicon wafer was first immersed in Cu plating solution followed by immersion in solution of HF and H_2O_2 to form micro-nanostructure roughness. The roughed surface was then treated with Teflon by spin coating to achieve a highly superhydrophobic surface which can be used for microfluid transportation and self-cleaning applications.

Nimittrakoolchai and Supothina [72] chemically etched the polyelectrolyte layer coated glass surface by HCl solution to develop microporous roughness. SiO_2 nanoparticles were then deposited followed by surface modification with trichloro (1*H*,1*H*,2*H*,2*H*-perfluorooctyl) silane to increase the contact angle of water to 152 ± 4 degrees. The prepared sample had a good antiadhesive property and high optical transparency property.

Varshney et al. [95] developed mechanically, chemically, UV, and thermally stable superhydrophobic coating on aluminum surface by chemically etching the surface with HCl followed by surface modification with lauric acid. The static water contact angle was measured to be 172 ± 5 degrees and sliding angle of 4 ± 0.5 degrees. The prepared sample exhibited good self-cleaning and antifogging property.

Kumar and Gogoi [96] etched the surface of aluminum with mixture of HCl and HNO_3 to form microstructure roughness. The roughed surface was further modified with hexadecyltrimethoxysilane (HDTMS) to make the surface superhydrophobic with water contact angle 162.0 ± 4.2 degrees and tilting angle of 4 ± 0.5 degrees with self-cleaning property. Besides this, the prepared sample was thermally, mechanically, and chemically stable.

Varshney et al. [97] prepared superhydrophobic steel mesh for oil-water separation. The sample was first chemically etched in a solution of hydrochloric acid and nitric acid followed by surface modification with lauric acid. The sample was mechanically, chemically, and thermally stable with static contact angle of 171 ± 4.5 degrees and a sliding angle of 4 ± 0.5 degrees.

Lomga et al. [98] synthesized self-cleaned, antifogged, and regenerable superhydrophobic aluminum surface by chemical etching with NaOH followed by surface modification with lauric acid. The prepared aluminum surface exhibited water contact angle of 170 degrees and sliding angle of 5 degrees. The prepared sample was mechanically and thermally stable. The sample was able to regenerate its property by immersing the sample in lauric solution.

Varshney et al. [99] developed superhydrophobic coating on aluminum surface by chemical etching with acid mixture of hydrochloric and nitric acids. The etched surface was then immersed in lauric acid solution to make the surface superhydrophobic with static contact angle of 170 ± 3.9 degrees and sliding angle of 4 ± 0.5 degrees. The prepared sample showed good self-cleaning and antifogging properties. Besides this, the samples were stable to mechanical disturbances.

Varshney et al. [100] fabricated superhydrophobic surface with static contact angle of 153 degrees and tilting angle of 5 degrees. The aluminum surface was chemically etched with KOH solution and was then modified by immersing in lauric acid. The prepared superhydrophobic aluminum surface showed self-cleaning and anticorrosive property. Besides this, the sample showed good mechanical, thermal, and UV stability.

3.6 Plasma-etching technique

It involves a high stream speed of glow discharge of an appropriate gas mixture being shot at a sample. The plasma generates volatile etch products and they etch the sample. Plasma treatment of surfaces can create micro/nanostructures. This technique has several advantages such as capability of automation, low material consumption, anisotropic, cheap, clean technique, chemical specific, and little damage to photoresist. It has several disadvantages such high capital investment, large number of process parameters to control (surface geometry, types of gases, flow rates, system conductance, radio frequency power to drive chemical reactions, water load, and patterning), resulting difficult to duplicate in other reactors, radiation from plasma causes surface damage, and poor pattern transfer and gases are quite toxic.

By employing plasma-etching technique, several studies have carried out for creating superhydrophobic surfaces. For example, Gao et al. [101] carried out two-step method in developing superhydrophobic zinc surface with water contact angle of 158 degrees and sliding angle <5 degrees. The surface was treated with glow discharge electrolysis plasma (GDEP) for etching and surface functionalization by stearic acid. The prepared sample exhibited good stability to different pH and long-term environmental exposure.

Barshilia and Gupta [102] prepared superhydrophobic (PTFE) surfaces plasma etching of the surface by argon and oxygen. The etched surface exhibited a water contact angle of 158 degrees after 4 h of treatment. These surfaces can be implemented in different applications in field of biomedical, biotechnological, and electrical insulation.

Youngblood and McCarthy [103] synthesized superhydrophobic surface on polypropylene surface with water contact angle of carried out 172 degrees. Polypropylene surface was simultaneously etched and was coated by PFTE using inductively coupled radio frequency argon plasma.

Balu et al. [104] achieved superhydrophobicity on different type of papers surfaces by plasma-enhanced etching and film deposition of pentafluoroethane that increased the contact angle to 159.4 degrees.

Teshima et al. [105] synthesized superhydrophobic coating on poly(ethylene terephthalate) substrates by two dry step method. The surface was first etched by selective oxygen plasma etching to develop nano texture surface roughness followed by surface modification by plasma-enhanced CVD of heptadecafluoro-1,1,2,2-tetrahydrodecyl-1-trimethoxysilane. The superhydrophobic surface has a contact angle of more than 150 degrees with good transparency property.

Psarski et al. [106] developed nanostructured epoxy/γ-Al_2O_3 nanoparticle composite by replicating the microstructures developed on aluminum surface by laser. The derived nanocomposite was then treated with air plasma for creating nanoroughness by etching. The etched surface was then modified by dip coating in 1*H*,1*H*,2*H*,2*H*-perfluorotetradecyltriethoxysilane to achieve a contact angle 160 degrees and sliding angle is 8 degrees.

3.7 Hydrothermal synthesis

Hydrothermal method is another technique used for synthesis of superhydrophobic and superliquiphobic coating. This technique is to produce crystalline substances from hot aqueous solution at high vapor pressure. This method is mostly used for creating roughness on the surface of substrate by using high temperature and high pressure. In this process, crystals are grown in an autoclave where materials along with water are supplied. Temperature gradient is created in between the opposite ends of autoclave chamber. Materials dissolve at hotter end and they are deposited on the seed crystals at cooler end, thus desired crystals grow. It can create crystalline phases which are not stable at the melting point. Materials those have high vapor pressure at or near their melting points can be grown by this method. It has ability to synthesize large crystals of high quality. This process has potential to contribute industrially due to its simple approach. However, it has inability to monitor crystals in the process of growth. The cost of equipment is also high.

By employing hydrothermal synthesis techniques, several works have been reported in literature. For example, Hao et al. [88] created the roughness on the surface of zinc by chemical etching with HCl followed by hydrothermal treatment with ammonium hydroxide. The roughed surface was further modified by perfluorooctanoic acid that showed both superhydrophobic and oleophobic property with contact angle of 151.85 degrees and 145.62 degrees for water and peanut oil, respectively.

Shen et al. [91] created different nanostructures by using different techniques on microstructured Ti_6Al_4V alloy surface. Nanostructures with nanowires were created by hydrothermal method, nanotubes by anodic oxidation, and nanomesh by two-step chemical reaction. The micro-nanostructured surface was then modified FAS-17 after which the contact angle of water increased to 161 degrees with tilting angle of 6 degrees.

Hu et al. [107] developed superhydrophobic glass surface with high adhesive force using two-step method. The surface was first coated with composite of carbon/silica. Carbon nanoparticles were developed on glass by hydrothermal method followed by depositing of SiO_2 prepared by hydrolysis. The surface was then modified by 1*H*,1*H*,2*H*,2*H*-perfluordecyltrimethoxysilane to increase the contact angle of water >150 degrees.

Xiao et al. [108] used hydrothermal method to fabricated superhydrophobic ZnO micro/nanocrystals assisted by PEG1000. The crystals developed were thermally and chemically stable with contact angle of water of 167 degrees.

Shi et al. [109] changed the surface of glass to superhydrophobic with water contact angle of 154 degrees and sliding angle lower than 3 degrees. The surface of glass was hydrothermally treated with solution of $Al(NO_3)_3 \cdot 9H_2O$, NaOH, and colloidal silica to develop rose like microstructures which were further modified by octyltrimethoxysilane to achieve superhydrophobicity.

3.8 Self-assembly technique

By this process, a disordered system of preexisting components assembles in an organized way or a sequence. This pattern is due to local noncovalent molecular interactions among the components themselves and without external direction. It is also known as molecular self-assembly when the constitutive components are molecules. It forms complex structures with minimal intervention. It grows the layer at low temperature without expensive equipment and tedious process. It has important implications with regards to the formation of thin-film technology. This type of surface modification method can be widely used on engineering metals. But this process is time consuming and mechanism is complex.

Several works have done for creating superhydrophobic surface. Yin et al. [110] etched the surface of copper by immersing the surface in a solution of sodium hydroxide and potassium persulfate solution to produce flower-like structure and nanoneedles of $Cu(OH)_2$. The roughed surface was then immersed in dodecanoic acid which forms self-assembled layer on the surface which increased the water contact angle to 153 degrees.

Pan et al. [111] synthesized UV resistant and laundering-resistant superhydrophobic cotton surface with contact angle of 146.27 degrees. The sample was first coated with nano-Al sol and which was further modified sodium stearate and stearic acid which formed self-assembly on the surfaces to make the surface superhydrophobic.

Li et al. [112] similarly prepared superhydrophobic coating of cotton surface. The sample was immersed in silica hydrosol followed by immersion in HDTMS. The HDTMS forms self-assembled monolayers (SAMs) on the roughed surface that increased the water contact angle to 151 degrees.

Song et al. [113] created superhydrophobic silicon surface by self-assembly method with contact angle of 153 degrees. Oxide layer was first prepared on the surface by chemical etching. The surface modification of etched surface was carried out by CVD of aminopropyltrimethoxysilane (APTMS) which forms SAM on the surface by reacting with —OH ions on the surface.

Yin et al. [114] created self-assembled gold nanoparticles and fullerene pyridyl derivatives thin gold films at water/toluene interface. The film exhibited superhydrophobic property with contact angle of 157 degrees having its applications in the fields of optical, electronic, biosensor, and catalytic materials due to its self-cleaning and self-repairing property.

Huaiyuan et al. [115] synthesized PTFE/polyetheretherketone (PEEK) composites with self-assembled octadecyltrichlorosilane (OTS) molecules modified potassium titanate whiskers (PTW). The sample showed water contact angle of 141 degrees and excellent mechanical, friction, and wear resistance.

Badre et al. [116] modified the surface of zinc layered with zinc oxide using different fatty acids like stearic acid, oleic acid, and elaidic acid. The prepared samples were stable to UV radiation and long-term environmental exposure with maximum contact angle of 167 degrees.

Nanda et al. [117] synthesized superhydrophobic/superoleophilic coating on steel mesh by etching the surface with mixture of $FeCl_3$ and HCl. The etched surface was then immersed in HDTMS which increased the static contact angle of water to 167 ± 3 degrees with sliding angle of 6 ± 1 degrees. The prepared sample exhibited good thermal, mechanical, and chemical stability with an excellent oil-water separation application.

Chauhan et al. [118] immersed the cotton substrate on the solution of HDTMS to increase the water contact angle to 157 ± 5 degrees with tilt angle of 7 degrees. The coating on cotton surface is due to the formation of SAM of HDTMS. The prepared sample was mechanically, chemically, thermally, and UV stable and was used for oil-water separation.

Panda et al. [119] developed superhydrophobic/superoleophobic coating on cotton surface by immersing the sample in a mixture of trichloro(octadecyl)silane and (pentafluorophenyl)triethoxy silane. These silanes reacts to the surface and forms a layer of low surface energy material which increased the contact angle to 172.9 ± 3 degrees, 169 ± 3 degrees, and 167 ± 3 degrees for water, ethylene glycol, and glycerol, respectively. The superhydrophobic coating also exhibited good thermal, chemical, mechanical, and UV stability and was used for self-cleaning and oil-water application.

Nanda et al. [120] synthesized superhydrophobic coating on glass surface by dip coating on the solution of OTS-modified SiO_2 microparticles. The surface energy of the glass was reduced to the monolayers of OTS on the surface. The prepared sample was chemically, thermally, and mechanically stable with static contact angle of 165.5 ± 5.7 degrees and hysteresis of 2.0 ± 0.5 degrees. The aforesaid superhydrophobic glass surface was used for self-cleaning application.

3.9 LBL deposition technique

The LBL deposition technique is a simple and cheap method to construct thin-film coatings by depositing alternating layers. It uses electrostatic interaction and covalent bonds to form multilayer grafts. This process can be used to produce a wide variety of materials including polymers, metals, ceramics, nanoparticles, and biological molecules.

By using this technique, several studies have carried out for creating superhydrophobic surfaces. For example, Lu et al. [121] synthesized superhydrophobic cotton fabric with UV-resistant and antibacterial property. The surface was coated by layer by layers of ZnBDC followed by immersing aqueous solution of sodium stearate to increase the water contact angle to 151.4 degrees.

Zhang et al. [76] synthesized superhydrophobic coating on ITO surface. The surface was first deposited by layer by layer of polyelectrolyte followed by electrodeposition of gold clusters. The roughed surface was then immersed in *n*-dodecanethiol solution for overnight to achieve superhydrophobic property with water contact angle maximum of 173 degrees.

Bravo et al. [122] developed superhydrophobic glass surface or silicon wafers with high transparency and antireflective property by LBL deposition method. A layer of adhesion layer followed by layers of SiO_2 nanoparticles of different size were coated on the surface that provided the desire roughness. The roughed surface was further modified by trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl) silane to reach a water contact angle of 160 degrees with sliding angle <10 degrees.

Amigoni et al. [123] deposited layer by layer of amino-functionalized silica nanoparticles and epoxy-functionalized smaller silica nanoparticles on glass surface. The prepared sample showed hierarchy structure and was further modified by (3-aminopropyl) trimethoxysilane to increase the water contact angle to 153 degrees and hysteresis of 12 degrees.

3.10 Lithography technique

This technique employs simple chemical processes to create an image. It produces two components: water repelling positive part and water retaining negative part. By this method different pattern including circular pillars, squared pillars, star-shaped pots, indented square pots of with different diameters, height, and spacing can be produced [124]. It is an expensive process. There are many ways in which lithography can be done. They are the following.

3.10.1 Photolithography

This process uses a mask of carrying the requisite pattern information and mask pattern that is to be transferred on the substrate by using some optical technique. It is widely used in integrated circuit manufacturing. It has three techniques: contact, proximity, and projection printing.

This process is not complex, simple, and fast. Small structures can be created with relatively inexpensive equipment. But this technique is limited due to mask wear, defect generation, and contamination. Mask required must be of same size that of substrate which increases the cost. It is also a slow process as it requires longer time to expose entire wafer. Moreover, it requires an environmental chamber for reducing noise, vibrations, controlling temperature, humidity, and this leads in increasing the cost of the process.

There are several published work on producing superhydrophobic coating using photolithography technique. For example, Oner and McCarthy [125] developed superhydrophobic coating on silicon wafers surface. Different lithographic pattern were created on silicon surface by photolithography followed by surface modification by dimethyldichlorosilane (DMDCS), *n*-octyldimethylchlorosilane (ODMCS), and heptadecafluoro-1,1,2,2-tetrahydrodecyldimethylchlorosilane (FDDCS) using vapor phase reaction. The contact angle of water was found to be 145 degrees, 143 degrees, and 150 degrees for DMDCS, ODMCS, and FDDCS, respectively.

3.10.2 Electron beam lithography

In this technique, surface roughness can be created by electron beam bombardment on the surface. The electron beam changes the solubility of resist, enabling selective removal of either the exposed/nonexposed regions of the resist by immersing it in solvent. It is a direct process to produce superhydrophobic surface where no mask is needed unlike photolithography, thus eliminating costs and time delay associated with mask production.

It is generally used to develop specialized and prototype devices. Besides, it is not an efficient process for industrial processing as it is complex, slow, and costly.

There is several published work on producing superhydrophobic coating using electron beam lithography technique. For example,

Feng et al. [126] created desired roughness of macroscopic hierarchical structure using electron beam lithography on wafer surfaces. The wafer surface changes to superhydrophobic with contact angle of 160 degrees after silanization with low surface energy.

Joki-Korpela et al. [127] developed antireflective polyurethane acrylate by solvent-free UV molding and fluoroalkylsilane modification which changed the wettability to hydrophobic and oleophobic in nature. The prepared acrylated was then replicated on the surface of PMMA by pair of nickel molds which was prepared by electron beam lithography and reaction ion etching.

3.10.3 X-Ray lithography

It is a process which uses X-rays to transfer a geometric pattern from a mask to a light-sensitive chemical photoresist on the substrate. A series of chemical treatments then engraves the produced patterns into the material under the photoresist. It has few advantages such as no diffraction effect, simple to use, no lens required, faster than electron beam lithography, uniform etching, and high resolution, applicable for large area. This technique can produce features at very small resolutions (lower than 10 nm). However, it has several disadvantages such as thin lens required, distortion in absorber, cannot be focused through lens, expensive mask, requires synchrotron facility, deformation and vibrations during the process, and time consuming.

Furstner et al. [34] studied the wetting and self-cleaning properties of three different specimen. First, a silicon wafer surface where spikes of regular pattern were obtained by X-ray lithography with surface modification by hexadecanthiol, second, replicate of water repelling leaves, and last metal foils which were hydrophobized by fluorinated agent. The silicon wafer with high spikes had a low sliding angle for which it can be applied in making self-cleaning surface from fog contamination.

3.10.4 Nano-imprint lithography

Nano-imprint lithography technique combines the speed of optical lithography with the resolution of electron beam lithography to make nanostructures on the surface. It creates coating by pressing and heating a thin film between a patterned template and surface. Due to heating, the patterned film adheres to the substrate. This technique can produce features at very small resolutions (lower than 10 nm) that cover a large area with a high throughput. It is relatively low-cost process and has commercial viability. This process is used in photodetectors, silicon quantum dots, quantum wires, and ring transistors. This process has been attracting attention from industries because it is used to mass-produce nanostructure product at low cost and high throughput. Although it is a flexible process but main barrier for the production of small resolutions is the development of mold.

Wu et al. [128] studied the most suitable conditions to deposit SAMs with antiadhesive capability for nanoimprint lithography. They developed nanostructures of concentric square recess molds on silicon wafers using e-beam writer. Two different samples of prepared silicon wafer were then produced by surface modification with liquid phase OTS and vapor phase perfluorodecyltrichlorosilane (FDTS) where it was observed that FDTS was preferred at high-temperature nanoimprinting than OTS due to its high thermal stability.

Zhang et al. [129] created the imprinting on the surface of silicon wafer coated with PS and PMMA films using a FDTS-treated molds. These surfaces form hierarchy structures with contact angle increasing to 128 degrees and 104 degrees for PS and PMMA film, respectively, thus making its application in different engineering materials.

Huang et al. [130] created nanostructures on plastic film by nanoimprinting using a template of anodized aluminum oxide (AAO). The developed nanoprinted plastic thin film reaches the contact angle of 130 degrees.

Pozzato et al. [131] carried out nanoimprint lithography and wet chemical etching on silicon surface with micron-scale dimensions. Resistance to etching by HF was done by positive photoresist and residual removal of resist layer in nanoimprint by UV-ozoner treatment. The surface was further modified by OTS which increased the water contact angle to 167 degrees.

3.10.5 Interference lithography

Interference lithography, also known as holographic lithography, is a technique for creating arrays of fine features on the substrate without the use of complex optical systems or photomasks. In this method, two or more coherent light waves with interference pattern between them are set up and are recorded in photoresist. These interference patterns have both intensity of maxima and minima in a periodic series. After exposing of surface to photolithographic processing, a pattern of periodic intensity emergences on the surface based on the photoresist.

Advantages of interference lithography are that it can produce dense features over a wide area at short period of time without loss of focus for which it is mainly used as testing photoresist processes for different new wavelengths used in lithography techniques. But there also lies some disadvantages of interference lithography such as it cannot be used for drawing patterns of arbitrary shapes because of its patterning feature. Besides this, non-optical effect, secondary electron in case of ionizing radiation and diffusion cannot be avoided.

Berendsen et al. [132] synthesized superhydrophobic thermoplastic polymer surface (PS and PMMA) by thermal imprint method followed by plasma polymerization of hexafluoropropene layer. Thermal imprinting was carried out by nickel stamp which was developed by customized laser interference lithography technique. The static water contact angle increased to 167 degrees with hysteresis below 5 degrees.

3.11 Template-assisted self-assembly

In this synthesis technique, a predefined structure (template) is introduced to self-assembly. In this method, colloidal are aggregated with controlled shape, size, and structures on the surface by removal of solvents from aqueous building blocks implemented on the patterned surface of two-dimensional (2D) arrays of templates. Colloidal particles get assembled according to the surface confinement provided by liquid droplets or by micro-fabricated to spherical objects by the building blocks. Colloidal crystals can also been grown on solid substrates by relieves in a patterned arrays.

Advantage of this process is that this method uses the combination of both lithography and self-assembly with their desirable aspects, that is, it controls the lithography as well as carried out self-assembly technique for which it has an upper hand as compared to both the techniques individually. It can produce different shape building blocks such as spheroid, cube, right bipyramid, and triangular with corner-to-corner junction. Template-assisted self-assembly (TASA) also provides flexibility in organizing the building blocks at nanoscale level because of its use of the capillary force.

Sun et al. [133] developed superhydrophobic glass surface by two simple techniques. The surface of glass was coated with micro and nanospheres silica by electrostatic absorbing technique and template directed self-assembly method. The surface was then modified with layer of fluoroalkylsilane that increased the water contact angle >160 degrees. The prepared coating can have its application in self-cleaning coating, microfluidic device, and thermal transfer apparatus.

Huaiyuan et al. [115] synthesized mechanical, friction, and wear-resistance coating with water contact angle of 141 degrees on PTW by PTFE/PEEK composites with self-assembled OTS.

3.12 Anodization

Anodization is a synthesis technique where a protective oxide layer of thickness 5–25 μm is developed on the surface of metal by electrolytic oxidation of metal surface in the presence of an acid. Besides, making the surface rough, the presence of oxide layer on anodized surfaces have high abrasion resistance and long-term stability as they do not get peel off from the surface even if at regular use. But the disadvantage of anodization technique is that it reduces the thermal conductivity of materials lower than the parent material. Also, colored anodized surface layer by organic dyes loses its color under sunlight after certain time of exposure.

Several works have been reported on superhydrophobicity using this technique. Liang et al. [134] developed chemically stable superhydrophilic/superhydrophobic coating on titanium surface. The Ti surface was anodized in acid solution containing HF and HNO_3 and water which changed the surface wettability to superhydrophilic. The anodized surface was then immersed in fluoroalkylsilane to make the surface superhydrophobic with water static contact angle of 160 degrees and sliding angle of 1.7 degrees.

Gao et al. [135] created complex micropore structure on the surface of Ti-6Al-4V alloy by anodization in the mixture of NaOH and H_2O_2 acid mixture. The etched surface wettability was made superhydrophobic by treating the surface with tridecafluoroctyltriethoxysilane which increased the water contact angle 158.5 ± 1.9 degrees and rolling angle of 5.3 ± 1.1 degrees. The prepared superhydrophobic surface was stable to air exposure, 3.5% NaCl solution and sand abrasion test.

Wang et al. [79] synthesized hierarchical structure by electrochemical deposition of nickel and copper on a template which was developed by APA. The deposit formed nanometer pillars in the pore of APA. The surface was then modified by FAS to obtain water contact angle of 152 degrees and sliding angle of 6 degrees for nickel and 157 degrees and a sliding angle of 3 degrees for copper.

Lee et al. [136] studied the water-droplet adhesiveness on aluminum surface. The AAO layers were fabricated by two-step anodization. The AAO was acid etched to change the roughness structure form nanopore to nanopillar arrays. The nanopillar roughed surface was further modified heptadecafluoro-1,1,2,2-tetrahydrodecyl-trichlorosilane to increase the water contact angle to 166.6 ± 1.2 degrees.

Yin et al. [137] synthesized anticorrosive, superhydrophobic aluminum surface by anodization in the presence of sulfuric acid. The anodized surface wettability was changed to superhydrophobic after modification with myristic acid with seawater contact angle of 154 degrees.

Vanithakumari et al. [138] achieved superhydrophobicity on titanium surface with contact angle of water of 150 degrees. The surface was first anodized in the presence of H_2SO_4 followed by surface modification by 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane. The prepared sample was stable to sea water and mild nitric acid solution.

3.13 Sol-gel process

Sol-gel technique is the most common method to synthesis superhydrophobic coating on different substrate surface. It is a method where colloidal particles with different sizes ranging from 1 to 100 nm are dispersed in gels that have an interconnected rigid network with pores size of submicrometer and polymeric chains of average length of $>1\ \mu m$. Here conversion of monomer takes place to colloidal solution (sol) that acts an initiator for integrated network (gel) for polymers or particles. The scale of the structure on surface ranging to nanoscale can be controlled at early stage of synthesis. This method is mainly used for bioinspired and bio-templating fabrications. The benefit of using this technique is it can be applied to any type of surfaces with homogenous coating as compared to traditional ceramic method. But the drawback of the coating technique is the large volume shrinkage, formation of crack while drying, increase in carbon content while using organic reagents during preparative step, densification during sintering and regular monitoring of process is essential.

Several studies have been carried out in synthesis of superhydrophobic coating on different surfaces using sol-gel method. For instance, Laksmi et al. [139] spray coated the sol-gel composite of fumed silica and perfluoroalkylmethacrylic copolymer in a hybrid sol-gel matrix on glass and aluminum surface. The prepared samples showed superhydrophobic and oleophobic property with contact angle of 158 degrees, 146 degrees, and 113 degrees for water, ethylene glycol, and lubricating oil, respectively. The repellency of oil was due to the presence of small amount of fluorine.

Fan et al. [140] developed superhydrophobic copper wafer with water contact angle 155.4 degrees. The surface of copper was first etched in acid solution followed by coating with sol-gel of vinyl trimethoxylsilane, ethanol, water, and ammonia water. The prepared sample remained stable in 3.5% NaCl solution making its application for self-cleaning and anticorrosive.

Lakshmi and Basu [141] synthesized superhydrophobic composite film with long stability on environmental exposure and tape peeling test. The sample was prepared by incorporating stearic acid modified colloidal zinc chloride fabricated in a sol-gel matrix. The prepared sample was then sprayed on glass surface which increased the water contact angle to 165 degrees and sliding angle <2 degrees.

Wang et al. [142] developed superhydrophobic wood surface with water contact angle of 164 degrees and tilting angle below 3 degrees. The surface was first immersed in a sol-gel TEOS, water, and NH_4OH, where the SiO_2 nanoparticles were deposited on wood surface. The deposited surface was then modified by 1*H*,2*H*,2*H*-perfluoroalkyltriethoxysilanes (POTS) using CVD to achieve superhydrophobicity. The prepared sample also exhibited good stability to ambient atmosphere.

Wang et al. [143] prepared a superhydrophobic sol-gel of trimethyl-modified silica particles. The sol-gel was then coated on canvas surface by LBL process of PTFE and superhydrophobic sol-gel. The water contact angle was measured be 153.3 ± 3.1 degrees and 152.3 ± 2.1 degrees after two and three bilayers. The prepared samples also exhibited self-cleaning property with excellent water impact test, tensile test, and accelerated weathering test.

Huang and Lin [144] developed superhydrophobic, transparent glass surface by coating the surface in a sol-gel of silicic acid and silica nanoparticles followed by coating with 1*H*,1*H*,2*H*,2*H*-perfluorooctyltrichlorosilane. The coated glass surface had a water contact angle >160 degrees and also showed good chemical and mechanical stability.

Su et al. [145] prepared a sol-gel of by-product of APS KH550 and polymethyl hydrosiloxane (PMHS) made from hydrolysis and condensation of the product. The prepared sol-gel was then coated on the surface of glass which showed water contact angle of 157 degrees and hysteresis angle is <1 degrees.

Wen et al. [146] fabricated superhydrophobic glass with water contact angle of 156 degrees and sliding angle of 5 degrees by coating sol-gel of methyltriethoxysilane (MTEOS)/TEOS/tri(isopropoxy)vinylsilane (TIPVS) in organic siloxane-modified polyacrylate emulsion (OSPA emulsion). The organic-inorganic derived sol-gel was produced by alkaline-catalyzed co-hydrolysis and copolycondensation reactions between tetraethoxysilane (TEOS), MTEOS, and TIPVS.

Lakshmi et al. [147] spray coated a sol-gel of silica nanoparticles embedded in hybrid sol-gel of MTEOS and colloidal silica produced due to partial condensation on glass surface. The prepared superhydrophobic glass surface exhibited a contact angle of 162.5 degrees with improved hardness.

Satapathy et al. [148] developed superhydrophobic glass surface by dip coating sol-gel of SiO_2 nanoparticles embedded in linear low-density polyethylene (LLDPE) polymer matrix. Different samples of porous (using ethanol as nonsolvent) and nonporous matrix were developed. The porous SiO_2 nanoparticles embedded in LLDPE showed a water contact angle of 170 degrees and tilting angle of 3.8 degrees. Besides this, the sample also exhibited good thermal, mechanical, and chemical stability with an excellent self-cleaning property.

Nanda et al. [149] synthesized self-cleaning superamphiphobic (both superhydrophobic and superoleophobic) coating on steel surface by casting the sol-gel solution of PFOTS-modified SiO_2 nanoparticle. The coated sample showed a contact angle of 167.0 ± 3.1 degrees, 165.0 ± 3.7 degrees, 164.0 ± 4.0 degrees, and 157.1 ± 2.1 degrees with sliding angles of 2.5 ± 0.5 degrees, 4.0 ± 0.5 degrees, 3.2 ± 0.5 degrees, and 5.6 ± 1 degrees for water, glycerol, ethylene glycol, and hexadecane, respectively. Superamphiphobic surface retained its property up to 350°C and also exhibited excellent chemical and mechanical stability.

Satapathy et al. [150] casted sol-gel of SiO_2 nanoparticles and LLDPE solution on filter paper to achieve superhydrophobicity with water contact angle of 167.8 ± 1.4 degrees and sliding angle of 3.8 ± 0.5 degrees for oil-water separation. The prepared sample also showed stability to mechanical, thermal, and chemical test.

3.14 Chemical vapor deposition

CVD technique has its wide application in materials-processing technology. In this method, the precursor is heated into gas form at high temperature and it then deposited on the surface of the substrate due to reaction with the hot surface and thus forms a thin-film layer on the surface. This technology is widely used in producing bulk materials and powders with high purity, deposition of materials on surface, and development of composite material via infiltration techniques. CVD technique is also used in fields of semiconductor and producing synthetic diamonds.

Advantage of using this process is it produces highly dense pure materials, uniform coating with good adhesion for complex-shaped components, surface morphology, crystal structure, and orientation can be controlled by controlling CVD parameters and use of wide range of chemicals deposition over a large spectrum of materials. Besides this, CVD techniques do have also some disadvantages such as use of toxic, corrosive, flammable, and explosive precursor gases can cause chemical and safety hazards and multicomponent component with proper stoichiometry is difficult to be coated because of their different vaporization rates [151].

Several works have been done on superhydrophobicity using CVD technique. For example, Rezaei et al. [152] synthesized superhydrophobic coating on glass, aluminum, and silicon slides using CVD technique. The surface were coated with TEOS, vinyltrimethoxysilane (VTMS), ammonia, and water which increased the contact angle of water above 160 degrees with hysteresis <5 degrees.

Wang et al. [153] coated the surface of PDMS film that showed water contact angle of 155.4 ± 2 degrees and sliding angle of 3.1 ± 0.3 degrees. ZnO nanocrystals were developed by CVD technique which was further modified by APS. The modified ZnO nanocrystals were then dispersed in PDMS to achieve superhydrophobic film.

Huang et al. [38] created aligned carbon nanotubes (CNT) on Fe-N coated Si substrate using CVD technique. The sample surface was then modified by ZnO thin film using filtered cathodic vacuum arc technique to achieve superhydrophobicity with water contact angle of 159 degrees.

4. Conclusions

Superhydrophobic coating has intense applications in the field of self-cleaning, antifogging, antibacteria, and environmental remediation because of its nonwetting behavior as water contact angle on these surfaces are >150 degrees. These surfaces are biomimic from the nature like lotus leaf, butterfly wings, skin of shark, etc. In this chapter, idea regarding the superhydrophobic surfaces has been discussed. It also provides the idea about the different models, that is, Wenzel model and Cassie-Baxter model governing on superhydrophobic surfaces. Different techniques for synthesis of artificial superhydrophobic coatings with their advantages and disadvantages are also discussed.

References

[1] M. Nosonovsky, B. Bhushan, Superhydrophobic surfaces and emerging applications: non-adhesion, energy, green engineering, Curr. Opin. Colloid Interface Sci. 14 (2009) 270–280.

[2] P.A. Levkin, F. Svec, J.J.M. Frechet, Porous polymer coatings: a versatile approach to superhydrophobic surfaces, Adv. Funct. Mater. 19 (2009) 1993–1998.

[3] B. Bhushan, Y.C. Jung, K. Koch, Self-cleaning efficiency of artificial superhydrophobic surfaces, Langmuir 25 (2009) 3240–3248.
[4] X. Zhang, F. Shi, J. Niu, Y.G. Jiang, Z.Q. Wang, Superhydrophobic surfaces: from structural control to functional application, J. Mater. Chem. 18 (2008) 621–633.
[5] J.R. Dorvee, A.M. Derfus, S.N. Bhatia, M.J. Sailor, Manipulation of liquid droplets using amphiphilic, magnetic one-dimensional photonic crystal chaperones, Nat. Mater. 3 (2004) 896–899.
[6] K.Y. Suh, M.C. Park, P. Kim, Capillary force lithography: a versatile tool for structured biomaterials interface towards cell and tissue engineering, Adv. Funct. Mater. 19 (2009) 2699–2712.
[7] B. Bhushan, Y.C. Jung, Natural and biomimetic artificial surfaces for superhydrophobicity self-cleaning, low adhesion, and drag reduction, Prog. Mater. Sci. 56 (2011) 1–108.
[8] T. Wagner, C. Neinhuis, W. Barthlott, Wettability and contaminability of insect wings as a function of their surface sculptures, *Acta Zool.* 77 (1996) 213–225.
[9] A.R. Parker, C.R. Lawrence, Water capture from desert fogs by a Namibian beetle, Nature 414 (2001) 33–34.
[10] X. Gao, L. Jiang, Biophysics: water-repellent legs of water striders, Nature 432 (2004) 36.
[11] D. Byun, J. Hong, J.H.K. Saputra, Y.J. Lee, H.C. Park, B.K. Byun, J.R. Lukes, Wetting characteristics of insect wing surfaces, J. Bionic Eng. 6 (2009) 63–70.
[12] K. Koch, B. Bhushan, W. Barthlott, Diversity of structure, morphology and wetting of plant surfaces, Soft Matter 4 (2008) 1943–1963.
[13] A. Nakajima, K. Hasimoto, T. Watanabe, Recent studies on super-hydrophobic films, *Monatsh. Chem.* 132 (2001) 31–41.
[14] H.Y. Erbil, A.L. Demirel, Y. Avci, O. Mert, Transformation of a simple plastic into a superhydrophobic surface, Science 299 (2003) 1377–1380.
[15] H. Li, X. Wang, Y. Song, Y. Liu, Q. Li, L. Jiang, D. Zhu, Super-amphipholic aligned carbon nanotube films, Angew. Chem. Int. 40 (2001) 1743–1746.
[16] T. Sun, G. Wang, H. Liu, L. Feng, L. Jiang, D. Zhu, Control over the wettability of an aligned carbon nanotube film, *J. Am. Chem. Soc.* 125 (2003) 14996–14997.
[17] Y. Wu, H. Sugimura, Y. Inoue, O. Takai, Thin films with nanotextures for transparent and ultra water-repellent coatings produced from trimethylmethoxysilane by microwave plasma CVD, Chem. Vap. Depos. 8 (2002) 47–50.
[18] N.J. Shirtcliffe, G. McHale, M.I. Newton, C.C. Perry, Intrinsically super hydrophobic organo-silica sol-gel foams, Langmuir 19 (2003) 5626–5631.
[19] C. Guo, L. Feng, J. Zhai, G. Wang, Y. Song, L. Jiang, D. Zhu, Large area fabrication of a nanostructure induced hydrophobic surface from a hydrophilic polymer, Chem. Phys. Chem. 5 (2004) 750–753.
[20] W. Lee, M.K. Jin, W.C. Yoo, J.K. Lee, Nanostructuring of a polymeric substrate with well-defined nanometer-scale topography and tailored surface wettability, Langmuir 20 (2004) 7665–7669.
[21] J.T. Han, X.R. Xu, K.W. Cho, Diverse access to artificial superhydrophobic surfaces using block co-polymers, Langmuir 21 (2005) 6662–6665.
[22] N.J. Shirtcliffe, G. McHale, M.I. Newton, G. Chabrol, C.C. Perry, Dual-scale roughness produces unusually water-repellent surfaces, Adv. Mater. 16 (2004) 1929–1932.
[23] H.S. Hwang, S.B. Lee, I. Park, Fabrication of raspberry-like superhydrophobic hollow silica particles, *Mater. Lett.* 64 (2010) 2159–2162.
[24] Y.H. Huang, J.T. Wu, S.Y. Yang, Direct fabricating patterns using stamping transfer process with PDMS mold of hydrophobic nanostructures on surface of micro-cavity, Microelectron. Eng. 88 (2011) 849–854.
[25] T. Yang, H. Tian, Y. Chen, Preparation of superhydrophobic silica films with honeycomb-like structure by emulsion method, J. Sol-Gel Sci. Technol. 49 (2009) 243–246.
[26] H. Kinoshita, A. Ogasahara, Y. Fukuda, N. Ohmae, Superhydrophobic/superhydrophilic micropatterning on a carbon nanotube film using a laser plasma-type hyperthermal atom beam facility, Carbon 48 (2010) 4403–4408.
[27] Z.G. Guo, J. Fang, J.C. Hao, Y.M. Liang, W.M. Liu, A novel approach to stable superhydrophobic surfaces, *Chem. Phys. Chem.* 7 (2006) 1674–1677.
[28] K.K. Lau, J. Bico, K.B.K. Teo, M. Chhowalla, G.A.J. Amaratung, W.I. Milne, G.H. McKinley, K. K. Gleason, Superhydrophobic carbon nanotube forests, Nano Lett. 3 (2003) 1701–1705.

[29] F. Mumm, A.T.J. van Helvoort, P. Sikoski, An easy route to superhydrophobic copper based droplet microfluidic systems, ACS Nano 3 (2009) 2647–2652.
[30] S.S. Latthe, H. Imai, V. Ganesan, A.V. Rao, Superhydrophobic silica films by sol-gel co-precursor method, Appl. Surf. Sci. 256 (2009) 217–222.
[31] V.V. Ganbavle, U.K.H. Bangi, S.S. Latthe, S.A. Mahadik, A.V. Rao, Self-cleaning silica coatings on glass by single step sol-gel route, Surf. Coat. Technol. 205 (2011) 5338–5344.
[32] S.S. Latthe, H. Hirashima, A.V. Rao, TEOS based water repellent silica films obtained by a co-precursor sol-gel method, Smart Mater. Struct. 18 (2009) 1–6.
[33] A.V. Rao, S.S. Latthe, C. Kappenstein, V. Ganesan, M.C. Rath, S.N. Sawant, Wetting behavior of high energy electron irradiated porous superhydrophobic silica films, *Appl. Surf. Sci.* 257 (2011) 3027–3032.
[34] R. Furstner, W. Barthlott, C. Neinhuis, P. Walzel, Wetting and self-cleaning properties of artificial superhydrophobic surfaces, Langmuir 21 (2005) 956–961.
[35] M. Ma, Y. Mao, M. Gupta, K.K. Gleason, G.C. Rutledge, Superhydrophobic fabrics produced by electrospinning and chemical vapor deposition, Macromolecules 38 (2005) 9742–9748.
[36] X. Zhang, Y. Guo, P. Zhang, Z. Wu, Z. Zhang, Superhydrophobic CuO-Cu2S nanoplate vertical arrays on copper surfaces, *Mater. Lett.* 64 (2010) 1200–1203.
[37] H. Liu, L. Feng, J. Zhai, L. Jiang, D.B. Zhu, Reversible wettability of a chemical vapor deposition prepared ZnO film between superhydrophobicity and superhydrophilicity, Langmuir 20 (2004) 5659–5661.
[38] L. Huang, S.P. Lau, H.Y. Yang, E.S.P. Leong, S.F. Yu, S. Prawer, Stable superhydrophobic surface via carbon nanotubes coated with a ZnO thin film, J. Phys. Chem. B 109 (2005) 7746–7748.
[39] L.B. Zhu, Y.H. Xiu, J.W. Xu, P.A. Tamirisa, D.W. Hess, C.P. Wong, Superhydrophobicity on two-tier rough surfaces fabricated by controlled growth of aligned carbon nanotube arrays coated with fluoro-carbon, Langmuir 21 (2005) 11208–11212.
[40] R.N. Wenzel, Resistance of solid surfaces to wetting by water, Ind. Eng. Chem. 28 (1936) 988–994.
[41] A.B.D. Cassie, S. Baxter, Wettability of porous surface, Trans. Faraday Soc. 40 (1944) 546–551.
[42] A. Lafuma, D. Quere, Superhydrophobic states, Nat. Mater. 2 (2003) 457–460.
[43] M. Reyssat, J.M. Yeomans, D. Quere, Impalement of fakir drop, Europhys. Lett. 81 (2008) 1–5.
[44] M. Reyssat, A. Pepin, F. Marty, Y. Chen, D. Quere, Bouncing transitions on microtextured materials, Europhys. Lett. 74 (2006) 306–312.
[45] D. Bartolo, F. Bouamrirene, E. Verneuil, A. Buguin, P. Silberzan, S. Moulinet, Bouncing or sticking droplets: impalement transitions on superhydrophobic micropatterned surfaces, Europhys. Lett. 74 (2006) 299–305.
[46] X. Zhang, Y. Guo, Z. Zhang, P. Zhang, Self-cleaning superhydrophobic surface based on titanium dioxide nanowires combined with polydimethylsiloxane, Appl. Surf. Sci. 284 (2013) 319–323.
[47] Z. Cui, L. Yin, Q. Wang, J. Ding, Q. Chen, A facile dip-coating process for preparing highly durable superhydrophobic surface with multi-scale structures on paint films, J. Colloid Interface Sci. 337 (2009) 531–537.
[48] R.J. Klien, P.M. Bieshuevel, B.C. Yu, C.D. Meinhart, F.F. Lange, Producing superhydrophobic surfaces with nanosilica spheres, Z. Metallkd. 94 (2003) 377–380.
[49] U. Cengiz, H.Y. Erbil, Superhydrophobic perfluoropolymer surfaces having heterogeneousroughness created by dip-coating from solutions containing a non-solvent, Appl. Surf. Sci. 292 (2014) 591–597.
[50] S.A. Mahadik, V. Parale, R.S. Vhatkara, D.B. Mahadik, M.S. Kavale, P.B. Wagh, S. Gupta, J. Gurav, Superhydrophobic silica coating by dip coating method, Appl. Surf. Sci. 277 (2013) 67–72.
[51] M. Ramezani, M.R. Vaezi, A. Kazemzadeh, Preparation of silane-functionalized silica films via two-step dip coating sol–gel and evaluation of their superhydrophobic properties, Appl. Surf. Sci. 317 (2014) 147–153.
[52] L. Gao, J. He, A facile dip-coating approach based on three silica sols to fabrication of broadband anti-reflective superhydrophobic coatings, J. Colloid Interface Sci. 400 (2013) 24–30.
[53] T. Liu, F. Zhang, C. Xue, L. Li, Y. Yin, Structure stability and corrosion resistance of nano-TiO_2 coatings on aluminum in seawater by a vacuum dip-coating method, Surf. Coat. Technol. 205 (2010) 2335–2339.

[54] A.V. Rao, A.B. Gurav, S.S. Latthe, R.S. Vhatkar, H. Imai, C. Kappenstein, P.B. Wagh, S. C. Gupta, Water repellent porous silica films by sol–gel dip coating method, J. Colloid Interface Sci. 352 (2010) 30–35.

[55] D. Nanda, P. Varshney, M. Satapathy, S.S. Mohapatra, B. Bhushan, A. Kumar, Single step method to fabricate durable superliquiphobic coating on aluminum surface with self-cleaning and anti-fogging properties, *J. Colloid. Interfacial Sci*. 507 (2017) 397–409.

[56] J. Sun, F. Zhang, J. Song, L. Wang, Q. Qu, Y. Lu, I. Parkin, Electrochemical fabrication of superhydrophobic Zn surfaces, *Appl. Surf. Sci*. 315 (2014) 346–352.

[57] V. Senez, V. Thomy, R. Dufour, Nanotechnologies for Synthetic Super Non-wetting Surfaces, John Wiley and Sons, Inc, 2014.

[58] C.K. Soz, E. Yilgor, I. Yilgor, Influence of the average surface roughness on the formation of superhydrophobic polymer surfaces through spin-coating with hydrophobic fumed silica, Polymer 62 (2015) 118–128.

[59] F. Zhang, M. Sun, S. Xu, L. Zhao, B. Zhang, Fabrication of oriented layered double hydroxide films by spin coating and their use in corrosion protection, Chem. Eng. J. 141 (2008) 362–367.

[60] A. Eskandari, P. Sangpour, M.R. Vaezi, Hydrophilic Cu_2O nanostructured thin films prepared by facile spin coating method: investigation of surface energy and roughness, Mater. Chem. Phys. 147 (2014) 1204–1209.

[61] J. Zhang, W. Zhang, N. Zhou, Y. Wenga, Z. Hu, Photoresponsive superhydrophobic surfaces from one-pot solution spin coating mediated by polydopamine, *RSC Adv*. 4 (2014) 24973–24977.

[62] L. Xu, R.G. Karunakaran, J. Guo, S. Yang, Transparent, superhydrophobic surfaces from one-step spin coating of hydrophobic nanoparticles, ACS Appl. Mater. Interfaces 4 (2012) 1118–1125.

[63] G. He, K. Wang, The super hydrophobicity of ZnO nanorods fabricated by electrochemical deposition method, Appl. Surf. Sci. 257 (2011) 6590–6594.

[64] H.K. Kim, Y.S. Cho, Fabrication of a superhydrophobic surface via spraying with polystyrene and multi-walled carbon nanotubes, Colloids Surf. A Physicochem. Eng. Asp. 465 (2015) 77–86.

[65] Y. Zhang, D. Ge, S. Yang, Spray-coating of superhydrophobic aluminum alloys with enhanced mechanical robustness, J. Colloid Interface Sci. 423 (2014) 101–107.

[66] Z. Cui, J. Ding, L. Scoles, Q. Wang, Q. Chen, Superhydrophobic surfaces fabricated by spray-coating micelle solutions of comb copolymers, *Colloid Polym. Sci*. 291 (2013) 1409–1418.

[67] J. Ma, X. Zhang, Y. Bao, J. Liu, A facile spraying method for fabricating superhydrophobic leather coating, Colloids Surf. A Physicochem. Eng. Asp. 472 (2015) 21–25.

[68] S.S. Latthe, A.V. Rao, Superhydrophobic SiO_2 micro-particle coatings by spray method, Surf. Coat. Technol. 207 (2012) 489–492.

[69] N.L. Tarwal, V.M. Khot, N.S. Harale, S.A. Pawar, S.B. Pawar, V.B. Patil, P.S. Patil, Spray deposited superhydrophobic ZnO coatings via seed assisted growth, Surf. Coat. Technol. 206 (2011) 1336–1341.

[70] L. Ovaskainen, I.R. Meizoso, N.A. Birkin, S.M. Howdle, U. Gedde, L. Wågberg, C. Turner, Towards superhydrophobic coatings made by non-fluorinated polymers sprayed from a supercritical solution, J. Supercrit. Fluids 77 (2013) 134–141.

[71] X.H. Xu, Z.Z. Zhang, J. Yanga, X.T. Zhu, Study of the corrosion resistance and loading capacity of superhydrophobic meshes fabricated by spraying method, Colloids Surf. A Physicochem. Eng. Asp. 377 (2011) 70–75.

[72] O.U. Nimittrakoolchai, S. Supothina, Deposition of organic-based superhydrophobic films for anti-adhesion and self-cleaning applications, J. Eur. Ceram. Soc. 28 (2008) 947–952.

[73] Y. Liu, S. Li, J. Zhang, Y. Wang, Z. Han, L. Ren, Fabrication of biomimetic superhydrophobic surface with controlled adhesion by electrodeposition, Chem. Eng. J. 248 (2014) 440–447.

[74] L. Cao, X. Lu, F. Pu, X. Yin, Y. Xia, W. Huang, Z. Li, Facile fabrication of superhydrophobic Bi/Bi_2O_3 surfaceswith hierarchical micro-nanostructures by electroless deposition or electrodeposition, Appl. Surf. Sci. 288 (2014) 558–563.

[75] Z. Zhao, H. Zhang, M. Zhao, W. Chen, X. Liu, Electrochemical Deposition and Superhydrophobic Behavior of $Cu(CH_3(CH_2)_{12}COO)_2$ on Stainless Steel, IEEE, 2011, pp. 283–286.

[76] X. Zhang, F. Shi, X. Yu, H. Liu, Y. Fu, Z. Wang, L. Jiang, X. Li, Polyelectrolyte multilayer as matrix for electrochemical deposition of gold clusters: toward super-hydrophobic surface, J. Am. Chem. Soc. 126 (2004) 3064–3065.

[77] M. Li, J. Zhai, H. Liu, Y. Song, L. Jiang, D. Zhu, Electrochemical deposition of conductive superhydrophobic zinc oxide thin films, J. Phys. Chem. B 107 (2003) 9954–9957.
[78] S.V. Gnedenkov, S.L. Sinebryukhov, V.S. Egorkin, D.V. Mashtalyar, A.M. Emelyanenko, L. B. Boinovich, Electrochemical properties of the superhydrophobic coatings on metals and alloys, J. Taiwan Inst. Chem. Eng. 45 (2014) 3075–3080.
[79] J. Wang, A. Li, H. Chen, D. Chen, Synthesis of biomimetic superhydrophobic surface through electrochemical deposition on porous alumina, *J. Bionic Eng.* 8 (2011) 122–128.
[80] M. Mahajan, S.K. Bhargava, A.P. O'Mullane, Electrochemical formation of porous copper 7,7,8,8-tetracyanoquinodimethane and copper 2, 3,5,6-tetrafluoro-7,7,8,8 tetracyanoquinodimethane honeycomb surfaces with superhydrophobic properties, Electrochim. Acta 101 (2013) 186–195.
[81] Y. Huang, D.K. Sarkar, X.G. Chen, Fabrication of superhydrophobic surfaces on aluminum alloy via electrodeposition of copper followed by electrochemical modification, Nano-Micro Lett. 3 (2011) 160–165.
[82] M. Han, Y. Park, J. Hyun, Y. Ahn, Facile method for fabricating superhydrophobic surface on magnesium, Bull. Kor. Chem. Soc. 31 (2010) 1067–1069.
[83] B. Qian, Z. Shen, Fabrication of superhydrophobic surfaces by dislocation-selective chemical etching on aluminum, copper, and zinc substrates, Langmuir 21 (2005) 9007–9009.
[84] Y.Y. Quan, P.G. Jiang, L.Z. Zhang, Development of fractal ultra-hydrophobic coating films to prevent water vapor dewing and to delay frosting, Fractals 22 (2014) 1440002 (1–12).
[85] D. Qi, N. Lu, H. Xu, B. Yang, C. Huang, M. Xu, L. Gao, Z. Wang, L. Chi, Simple approach to wafer-scale self-cleaning antireflective silicon surfaces, Langmuir 25 (2009) 7769–7772.
[86] Y. Shi-heng, Z. Bin, L. Yun-chun, Y. Ji, K. Tong-chun, Fabrication of superhydrophobic aluminum plate by surface etching and fluorosilane modification, Chem. Res. Chin. Univ. 28 (2012) 903–906.
[87] D. Xie, W. Li, A novel simple approach to preparation of superhydrophobic surfaces of aluminum alloys, *Appl. Surf. Sci.* 258 (2011) 1004–1007.
[88] L. Hao, Y. Sirong, H. Xiangxiang, L. Enyang, Z. Yan, Fabrication of superhydrophobic and oleophobic surface on zinc substrate by a simple method, Colloids Surf. A Physicochem. Eng. Asp. 469 (2015) 271–278.
[89] R. Liao, Z. Zuo, C. Guo, Y. Yuan, A. Zhuang, Fabrication of superhydrophobic surface on aluminum by continuous chemical etching and its anti-icing property, *Appl. Surf. Sci.* 317 (2014) 701–709.
[90] W. Liu, L. Sun, Y. Luo, R. Wub, H. Jiang, Y. Chena, G. Zeng, Y. Liu, Facile transition from hydrophilicity to superhydrophilicity and superhydrophobicity on aluminum alloy surface by simple acid etching and polymer coating, *Appl. Surf. Sci.* 280 (2013) 193–200.
[91] Y. Shen, H. Tao, S. Chen, Y. Xie, T. Zhou, T. Wang, J. Tao, Water repellency of hierarchical superhydrophobic Ti6Al4V surfaces improved by secondary nanostructures, *Appl. Surf. Sci.* 321 (2014) 469–474.
[92] X. Xu, Z.Z. Zhang, W.M. Liu, Stable biomimetic super-hydrophobic copper surface fabricated by a simple wet-chemical method, J. Dispers. Sci. Technol. 31 (2010) 488–491.
[93] P. Li, X. Chen, G. Yang, L. Yu, P. Zhang, Fabrication of a superhydrophobic etched copper–silver/stearic acid composite coating evaluation of its friction-reducing and anticorrosion abilities, Mater. Express 4 (2014) 309–316.
[94] J.P. Lee, S. Choi, S. Park, Extremely superhydrophobic surfaces with micro- and nanostructures fabricated by copper catalytic etching, Langmuir 27 (2011) 809–814.
[95] P. Varshney, J. Lomga, P.K. Gupta, S.S. Mohapatra, A. Kumar, Durable and regenerable superhydrophobic coatings for aluminium surfaces with excellent water-repellent self-cleaning and anti-fogging properties, Tribol. Int. 119 (2018) 38–44.
[96] A. Kumar, B. Gogoi, Development of durable self-cleaning superhydrophobic coatings for aluminium surfaces via chemical etching method, Tribol. Int. 118 (2018) 114–118.
[97] P. Varshney, D. Nanda, S.S. Mohapatra, A. Kumar, A facile modification of steel mesh for selective separation of oil-water mixtures, *New J. Chem.* 41 (2017) 7463–7471.
[98] J. Lomga, P. Varshney, D. Nanda, M. Satapathy, S.S. Mohapatra, A. Kumar, Fabrication of durable and regenerable superhydrophobic coatings with excellent self-cleaning and anti-fogging properties for aluminium surfaces, J. Alloys Compd. 712 (2017) 161–170.

[99] P. Varshney, S.S. Mohapatra, A. Kumar, Fabrication of mechanically stable superhydrophobic aluminium surface with excellent self-cleaning and anti-fogging properties, Biomimetics 2 (2017) 1–12.
[100] P. Varshney, S.S. Mohapatra, A. Kumar, Superhydrophobic coatings for aluminium surfaces synthesized by chemical etching process, Int. J. Smart Nano Mater. 7 (2016) 248–264.
[101] J. Gao, Y. Li, Y. Li, H. Liu, W. Yang, Fabrication of superhydrophobic surface of stearic acid grafted zinc by using an aqueous plasma etching technique, Cent. Eur. J. Chem. 10 (2012) 1766–1772.
[102] H.C. Barshilia, N. Gupta, Superhydrophobic polytetrafluoroethylene surfaces with leaf-like micro-protrusions through Ar + O_2 plasma etching process, Vacuum 99 (2014) 42–48.
[103] J.P. Youngblood, T.J. McCarthy, Ultrahydrophobic polymer surfaces prepared by simultaneous ablation of polypropylene and sputtering of poly(tetrafluoroethylene) using radio frequency plasma, Macromolecules 32 (1999) 6800–6806.
[104] B. Balu, J.S. Kim, V. Breedveld, D.W. Hess, Design of superhydrophobic paper/cellulose surfaces via plasma enhanced etching and deposition, in: Contact Angle, Wettability and Adhesion, vol. 6, Taylor & Francis Group, 2009, pp. 235–249.
[105] K. Teshima, H. Sugimura, Y. Inoue, O. Takai, A. Takano, Transparent ultra-water-repellent poly(ethylene terephthalate) substrates fabricated by oxygen plasma treatment and subsequent hydrophobic coating, *Appl. Surf. Sci.* 244 (2005) 619–622.
[106] M. Psarski, J. Marczak, J.B. Grobelny, G. Celichowski, Superhydrophobic surface by replication of laser micromachined pattern in epoxy/alumina nanoparticle composite, J. Nanomater. 2014 (2014) 1–11. Article ID 547895.
[107] R. Hu, G. Jiang, X. Wang, X. Xi, R. Wang, Facile preparation of superhydrophobic surface with high adhesive forces based carbon/silica composite films, Bull. Mater. Sci. 36 (2013) 1091–1095.
[108] C. Xiao, J. Yang, T. Li, Fabrication and superhydrophobic property of ZnO micro/nanocrystals via a hydrothermal route, *J. Nanomater.* 2014 (2014) 1–6. Article ID 680592.
[109] F. Shi, X. Chen, L. Wang, J. Niu, J. Yu, Z. Wang, X. Zhang, Roselike microstructures formed by direct in situ hydrothermal synthesis: from superhydrophilicity to superhydrophobicity, *Chem. Mater.* 17 (2005) 6177–6180.
[110] S. Yin, D. Wu, J. Yang, S. Lei, T. Kuang, B. Zhu, Fabrication and surface characterization of biomimic superhydrophobic copper surface by solution-immersion and self-assembly, Appl. Surf. Sci. 257 (2011) 8481–8485.
[111] C. Pan, L. Shen, S. Shang, Y. Xing, Preparation of superhydrophobic and UV blocking cotton fabric via sol–gel method and self-assembly, Appl. Surf. Sci. 259 (2012) 110–117.
[112] Z.X. Li, Y.J. Xing, J.J. Dai, Superhydrophobic surfaces prepared from water glass and non-fluorinated alkylsilane on cotton substrates, Appl. Surf. Sci. 254 (2008) 2131–2135.
[113] X. Song, J. Zhai, Y. Wang, L. Jiang, Self-assembly of amino-functionalized monolayers on silicon surfaces and preparation of superhydrophobic surfaces based on alkanoic acid dual layers and surface roughening, *J. Colloid Interface Sci.* 298 (2006) 267–273.
[114] G. Yin, W. Xue, F. Chen, X. Fan, Self-repairing and superhydrophobic film of gold nanoparticles and fullerene pyridyl derivative based on the self-assembly approach, Colloids Surf. A Physicochem. Eng. Asp. 340 (2009) 121–125.
[115] W. Huaiyuana, Z. Yanjia, F. Xin, L. Xiaohua, The effect of self-assembly modified potassium titanate whiskers on the friction and wear behaviors of PEEK composites, Wear 269 (2010) 139–144.
[116] C. Badre, P. Dubot, D. Lincot, T. Pauporte, M. Turmine, Effects of nanorod structure and conformation of fatty acid self-assembled layers on superhydrophobicity of zinc oxide surface, *J. Colloid Interface Sci.* 316 (2007) 233–237.
[117] D. Nanda, A. Sahoo, A. Kumar, B. Bhushan, Facile approach to develop durable and reusable superhydrophobic/superoleophilic coatings for steel mesh surfaces, J. Colloid Interface Sci. 535 (2019) 50–57.
[118] P. Chuahan, A. Kumar, B. Bhushan, Self-cleaning, stain-resistant and anti-bacterial superhydrophobic cotton fabric prepared by simple immersion technique, J. Colloid Interface Sci. 535 (2019) 66–74.
[119] A. Panda, P. Varshney, S.S. Mohapatra, A. Kumar, Development of liquid repellent coating on cotton fabric by simple binary silanization with excellent self-cleaning and oil-water separation properties, Carbohydr. Polym. 181 (2018) 1052–1060.

[120] D. Nanda, P. Varshney, M. Satapathy, S.S. Mohapatra, A. Kumar, Self-assembled monolayer of functionalized silica microparticles for self-cleaning applications, Colloids Surf. A Physicochem. Eng. Asp. 529 (2017) 231–238.

[121] L. Lu, C. Hu, Y. Zhu, H. Zhang, R. Li, Y. Xing, Multi-functional finishing of cotton fabrics by water-based layer-by-layer assembly of metal–organic framework, Cellulose 25 (2018) 4223–4238.

[122] J. Bravo, L. Zhai, Z. Wu, R.E. Cohen, M.F. Rubner, Transparent superhydrophobic films based on silica nanoparticles, Langmuir 23 (2007) 7293–7298.

[123] S. Amigoni, E.T. Givenchy, M. Dufay, F. Guittard, Covalent layer-by-layer assembled superhydrophobic organic-inorganic hybrid films, Langmuir 25 (2009) 11073–11077.

[124] E. Celia, T. Darmanin, E.T. Givenchy, S. Amigoni, F. Guittard, Recent advances in designing superhydrophobic surfaces, J. Colloid Interface Sci. 402 (2013) 1–18.

[125] D. Oner, T.J. McCarthy, Ultrahydrophobic surfaces. effects of topography length scales on wettability, Langmuir 16 (2000) 7777–7782.

[126] J.S. Feng, M.T. Tuominen, J.P. Rothstein, Hierarchical superhydrophobic surfaces fabricated by dual-scale electron-beam-lithography with well-ordered secondary nanostructures, *Adv. Funct. Matter.* 21 (2011) 3715–3722.

[127] F.J. Korpela, J. Karvinen, B. Päivänranta, A. Partanen, M. Suvanto, M. Kuittinen, T. T. Pakkanen, Hydrophobic and oleophobic anti-reflective polyacrylate coatings, Microelectron. Eng. 114 (2014) 38–46.

[128] C.W. Wu, Y.K. Shen, S.Y. Chuang, C.S. Wei, Anti-adhesive effects of diverse self-assembled monolayers in nanoimprint lithography, Sens. Actuators A Phys. 139 (2007) 145–151.

[129] F. Zhang, J. Chan, H.Y. Low, Biomimetic, hierarchical structures on polymer surfaces by sequential imprinting, Appl. Surf. Sci. 254 (2008) 2975–2979.

[130] C.F. Huang, Y. Lin, Y.K. Shen, Y.M. Fan, Optimal processing for hydrophobic nanopillar polymer surfaces using nanoporous alumina template, Appl. Surf. Sci. 305 (2014) 419–426.

[131] A. Pozzato, S.D. Zilio, G. Fois, D. Vendramin, G. Mistura, M. Belotti, Y. Chen, M. Natali, Superhydrophobic surfaces fabricated by nanoimprint lithography, Microelectron. Eng. 83 (2006) 884–888.

[132] C.W.J. Berendsen, M. Skeren, D. Najdek, F. Cerny, Superhydrophobic surface structures in thermoplastic polymers by interference lithography and thermal imprinting, Appl. Surf. Sci. 255 (2009) 9305–9310.

[133] C. Sun, L.Q. Ge, Z.Z. Gu, Fabrication of super-hydrophobic film with dual-size roughness by silica sphere assembly, Thin Solid Films 515 (2007) 4686–4690.

[134] J. Liang, K. Liu, D. Wang, H. Li, P. Li, S. Li, S. Su, S. Xu, Y. Luo, Facile fabrication of superhydrophilic/superhydrophobic surface on titanium substrate by single-step anodization and fluorination, Appl. Surf. Sci. 338 (2015) 126–136.

[135] Y. Gao, Y. Sun, D. Guo, Facile fabrication of superhydrophobic surfaces with low roughnesson Ti–6Al–4V substrates via anodization, Appl. Surf. Sci. 314 (2014) 754–759.

[136] W. Lee, B.G. Park, D.H. Kim, D.J. Ahn, Y. Park, S.H. Lee, K.B. Lee, Nanostructure-dependent water-droplet adhesiveness change in superhydrophobic anodic aluminum oxide surfaces: from highly adhesive to self-cleanable, Langmuir 26 (2010) 1412–1415.

[137] Y. Yin, T. Liu, S. Chen, T. Liu, S. Cheng, Structure stability and corrosion inhibition of superhydrophobic film on aluminum in seawater, Appl. Surf. Sci. 255 (2008) 2978–2984.

[138] S.C. Vanithakumari, R.P. George, U.K. Mudali, Influence of silanes on the wettability of anodized titanium, Appl. Surf. Sci. 292 (2014) 650–657.

[139] R.V. Lakshmi, T. Bharathidasan, P. Bera, B.J. Basu, Fabrication of superhydrophobic and oleophobic sol–gel nanocomposite coating, Surf. Coat. Technol. 206 (2012) 3888–3894.

[140] Y. Fan, C. Li, Z. Chen, H. Chen, Study on fabrication of the superhydrophobic sol–gel films based on copper wafer and its anti-corrosive properties, Appl. Surf. Sci. 258 (2012) 6531–6536.

[141] R.V. Lakshmi, B.J. Basu, Fabrication of superhydrophobic sol–gel composite films using hydrophobically modified colloidal zinc hydroxide, J. Colloid Interface Sci. 339 (2009) 454–460.

[142] S. Wang, C. Liu, G. Liu, M. Zhang, J. Li, C. Wang, Fabrication of superhydrophobic wood surface by a sol–gel process, Appl. Surf. Sci. 258 (2011) 806–810.

[143] S.D. Wang, B.J. Lin, C.C. Hsieh, C.C. Lin, Application of superhydrophobic sol gel on canvas, Appl. Surf. Sci. 307 (2014) 101–108.
[144] W.H. Huang, C.S. Lin, Robust superhydrophobic transparent coatings fabricated by a low-temperature sol–gel process, Appl. Surf. Sci. 305 (2014) 702–709.
[145] D. Su, C. Huang, Y. Hu, Q. Jiang, L. Zhang, Y. Zhu, Preparation of superhydrophobic surface with a novel sol–gel system, Appl. Surf. Sci. 258 (2011) 928–934.
[146] X.F. Wen, K. Wang, P.H. Pi, J.X. Yang, Z.Q. Cai, L. Zhang, Y. Qian, Z.R. Yang, D. Zheng, J. Cheng, Organic–inorganic hybrid superhydrophobic surfaces using methyltriethoxysilane and tetraethoxysilane sol–gel derived materials in emulsion, Appl. Surf. Sci. 258 (2011) 991–998.
[147] R.V. Lakshmi, T. Bharathidasan, B.J. Basu, Superhydrophobic sol–gel nanocomposite coatings with enhanced hardness, Appl. Surf. Sci. 257 (2011) 10421–10426.
[148] M. Satapathy, P. Varshney, D. Nanda, S.S. Mohapatra, A. Behera, A. Kumar, Fabrication of durable porous and non-porous superhydrophobic LLDPE/SiO_2 nanoparticles coatings with excellent self-cleaning property, Surf. Coat. Technol. 341 (2018) 31–39.
[149] D. Nanda, T. Swetha, P. Varshney, P.K. Gupta, S.S. Mohapatra, A. Kumar, Temperature dependent switchable superamphiphobic coating on steel surface, J. Alloys Compd. 727 (2017) 1293–1301.
[150] M. Satapathy, P. Varshney, D. Nanda, A. Panda, S.S. Mohapatra, A. Kumar, Fabrication of superhydrophobic and superoleophilic polymer composite coatings on cellulosic filter paper for oil-water separation, Cellulose 24 (2017) 4405–4418.
[151] K.L. Choy, Chemical vapour deposition of coatings, Prog. Mater. Sci. 48 (2003) 57–170.
[152] S. Rezaei, I. Manoucheri, R. Moradian, B. Pourabbas, One-step chemical vapor deposition and modification of silica nanoparticles at the lowest possible temperature and superhydrophobic surface fabrication, Chem. Eng. J. 252 (2014) 11–16.
[153] B.B. Wang, J.T. Feng, Y.P. Zhao, T.X. Yu, Fabrication of novel superhydrophobic surfaces and water droplet bouncing behavior — Part 1: stable ZnO–PDMS superhydrophobic surface with low hysteresis constructed using ZnO nanoparticles, J. Adhes. Sci. Technol. 24 (2010) 2693–2705.