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Recent Advances in the Methods for Designing Superhydrophobic Surfaces

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Abstract

The investigations of superhydrophobicity and self-cleaning surfaces have been given a lot of attention in the last few decades. The surfaces having water contact angle larger than 90° are termed as hydrophobic surfaces and those which exhibit contact angle higher than 150° are said to be superhydrophobic. Such surfaces were first observed in nature in various plants and animals, for example, lotus leaf-like structures. Water repellence of various materials have shown great influences on various applications such as self-cleaning, anti-ageing, water-oil separation, water corrosion in electrical industry, water proof textiles, controlled transportation of fluids, etc. Generally, surface micro/nanostructuring combined with low surface energy of materials leads to extreme anti-wetting properties. The hundreds of research articles and more than 450 patents on the subject of nature mimicking self-cleaning surfaces prove the potential of this topic.

Self-cleaning property depends on both surface morphology and surface chemistry. For achieving superhydrophobic surfaces, we can, typically, either increase the roughness of the intrinsically hydrophobic material or tune desired roughness and morphology on hydrophilic surfaces. Depending on such parameters a water droplet on the surface attains either Wenzel or Cassie-Baxter state.

For the preparation of superhydrophobic surfaces, various physical and chemical methods have been successfully used. Methods such as hydrothermal process, using various templates, plasma surface modifications, physical and chemical vapour deposition, layer by layer deposition, electrospinning and sol-gel processing have been used for achieving desired roughness and surface chemistry on various

substrates. In this field of research, various fabrication methods have significant role in deciding the extent of superhydrophobic behaviour of the surface, depending on the material which is used for the processing. In this chapter, the most recent developments in various methods used for fabricating superhydrophobic surfaces are presented along with their advantages and limitations.

Keywords: Superhydrophobicity, natural mimics, self-cleaning, hierarchical structure

1. Introduction

Wetting properties of various solid surfaces with various polar and non-polar solvents are getting attention in recent decades because of the increased demand for them in various fields of applications. Superhydrophilicity and superhydrophobicity are two important terms used to explain the wetting behaviour of solid surfaces. Any surface which allows the spreading of a water droplet to provide a contact angle value below 5° is called superhydrophilic surface, whereas the criteria for the surface to be superhydrophobic is to get the water contact angle to a value above 150° [1]. On the other hand, observed values of static contact angle measurements depend on the used fitting mode [2]. For a proper comparison, one should repeatedly use the same volume of water droplet since the volume can also affect the measurement results. In addition, contact angle hysteresis needs to be taken into consideration because hydrophobic surfaces are widely used for self-cleaning applications. Contact angle hysteresis is defined as the difference between the advancing and receding contact angles. The lower the value, the easier the drop will roll off from the surface.

The idea of hydrophobic surfaces came from nature itself —observing the self-cleaning ability of plant leaves and animal wings to roll off water droplet from the surface, termed as lotus effect. The naturally occurring hydrophobic surfaces achieve the high contact angle values because of the rough surfaces coated with the low surface energy wax, which has high repelling interactions with the polar solvents including water [3]. Many such surfaces have a coating composed of particles with size ranging from 20-40 μm , with or without hierarchical structures to provide additional surface area [4]. To explain the stability of the water drop on the surfaces there are two major theories put forward in which the water exists in either Wenzel or Cassie state. In Wenzel model, the water drop fit inside the grooves of the rough surface [Figure 1A] and is described by equation 1,

$$\gamma_{lv} \cos \theta_w = r(\gamma_{sv} - \gamma_{sl}) \quad (1)$$

where θ_w is the water contact angle, r is the roughness factor and γ_{lv} , γ_{sv} and γ_{sl} are the different surface tensions involved in the system (liquid/vapour, solid/vapour and solid/liquid, respectively) [5].

In Cassie state, the droplet is stabilized on the top of a surface by the air pockets in between the grooves (Figure 1B) following the equation 2,

$$\cos\theta_c = -1 + f_s \left(\frac{L}{l} \right)^{D-2} (\cos\theta + 1) \quad (2)$$

where θ_c is the contact angle correlated to the chemical heterogeneity, f_s is the area fractions of solid material, L and l are the upper and lower limits of fractal behaviour and D is the fractal dimension [6].

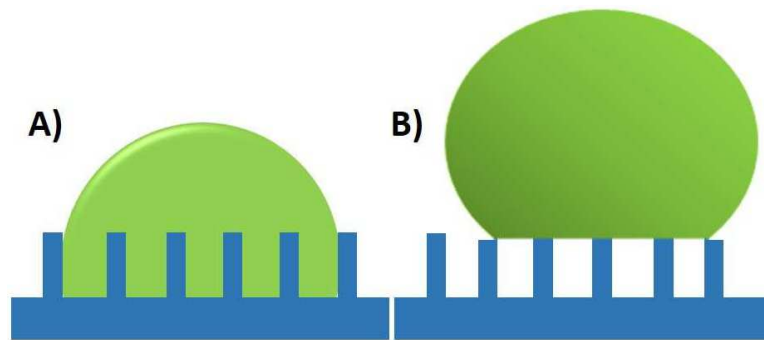


Figure 1. Existence of water droplet on a rough surface: A) Wenzel state, B) Cassie state.

There are some reports which questions the co-existence of both Wenzel and Cassie states. However, these two models are well accepted to explain the existence of solvent on a solid surface [7].

2. Methods for generating superhydrophobic surfaces

The water repelling ability of various materials have shown great influence on various applications such as self-cleaning, anti-ageing, water-oil separation, water corrosion in electrical industry, water proof textiles, controlled transportation of fluids, etc. [2, 4, 8, 9]. Generally, surface micro/nanostructuring combined with low surface energy of materials leads to extreme anti-wetting properties. Hundreds of research articles and more than 450 patents on the subject of nature mimicking self-cleaning surfaces show the potential of this topic. For the fabrication of superhydrophobic surfaces, various physical and chemical methods have been used. Methods such as templating, plasma surface modifications, physical and chemical deposition, layer by layer deposition, electrospinning, hydrothermal process and sol-gel processing have been used for achieving desired roughness and surface chemistry on various substrates. The texturing and coating are explained in short in the following text on the basis of very recent articles in terms of application point of view to give the reader a general idea of the field.

Method	Reference
Templating	[3, 10-23]
Electrospinning	[24-35]
Hydrothermal synthesis	[38-44]
Sol-Gel	[45-52]
Layer by layer method	[45, 54-61]
Physical and chemical vapour deposition methods	[4, 23, 62-70, 85-88]
Plasma etching	[3, 45, 75-79]

Table 1. List of recent publications on various methods for creating anti-wetting surfaces

2.1. Templating

Templating method refers to the copying of a rough surface with superhydrophobic properties. With this technique, a suitable 2D or 3D surface pattern is filled with certain soft material as the first step, then the material is hardened and the template removed by a suitable method keeping the replica intact [10]. The main advantage of this method is that it is very easy to copy water repelling natural surfaces in a large-scale level. This method is comparatively cheap and very suitable for patterning soft materials such as polymers where, in most of the cases, the template can be recycled [10]. Feng et al. created fine superhydrophobic nano fibre structures of poly vinyl alcohol (PVA) with aluminium oxide membrane as a template [11]. When the PVA precursors were extruded in solution through the nano porous template membrane, the polymer molecules underwent an alignment with the hydrophobic methylene groups pointing towards the external environment. A number of factors, including intermolecular hydrogen bonding, made it possible to attain a superhydrophobic surface of an amphilic material. Superhydrophobic polymer materials, especially those that have large surface area, are interesting for large-scale applications for separating hydrocarbon solvents from water, oil from water sources, etc. [12]. By applying a suitable soft material we can directly replicate the topography of various naturally occupying superhydrophobic surfaces. For example, *Xanthosoma Sagittifolium* leaf template was used to create electroactive epoxy surface to increase the water contact angle from 81° to 155° [13]. The comparison of the SEM images of the template and the replica is presented in Figure 2.

On the other hand, heat and pressure-driven nanostructuring on the polystyrene substrate with alumina template gave raise to specifically aligned nanoemboss, nanopost array with embossed base and aligned polymer nanofibres. Such nanofibres with small aspect ratio resembled the wings of *Cicada orni*, which has the self-dust cleaning capability achieved by the sculptured nanostructures on the surface, whereas the nanofibres with reasonably high aspect ratio showed self-cleaning ability towards water droplets. By using the same methodology, with additionally applied pressure, polymer materials have been nanostructured to achieve contact angle above 150° [14]. Template-assisted methods are also known for designing 3D ordered superhydrophobic microstructures from water insoluble materials (including

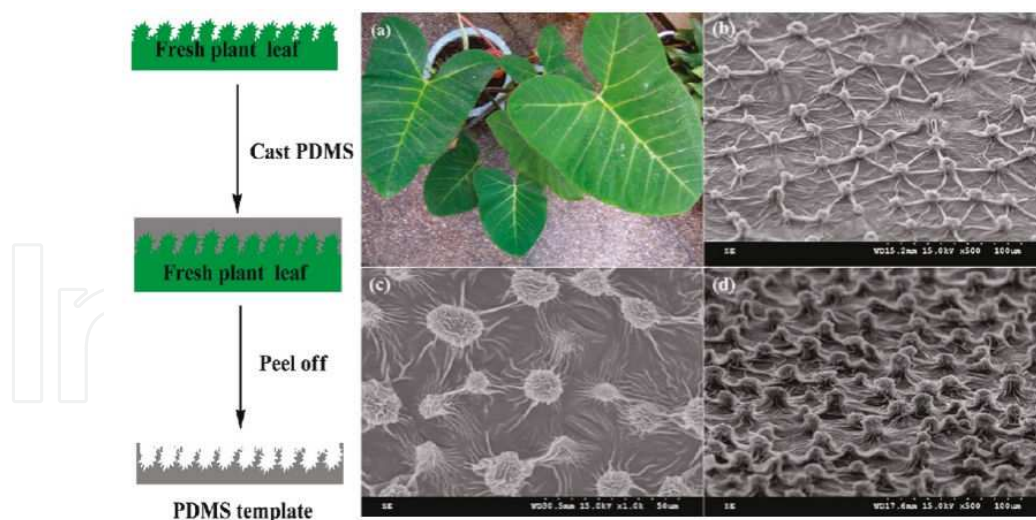


Figure 2. Schematic of the processing method and (a) Photograph of the *Xanthosoma Sagittifolium* leaves. (b) SEM image of the leaf. (c) SEM images of the imprinted layers of composite showing a top view of the surface. (d) SEM images of the imprinted layers of composite showing a cross-section view of the surface. [Reproduced with the permission of American Chemical Society, *Chem. Mater.* 2011, 23, 2075-2083]

polytetrafluoroethylene), which are promising as a host cage for various organic and inorganic materials for nanostructuring [15].

However, the template removing step — especially for delicate materials including polymers — can be really challenging since it is associated with high temperature processes or strong chemical etch [15, 16]. Exposure to non-friendly chemicals or to very high temperature can easily disorder the mesostructures or make unfavourable chemical changes to the polymer chains. To avoid these complications, use of easily removable templates is preferred. The new developments in the field focus on templates which undergo chemical changes and completely disappear or are naturally removed from the replica into the reaction medium. For instance, various metal oxide templates are utilized as a catalyst for the polymerisation process, where the metal undergoes change in oxidation state with the progress of reaction and completely converts into a water soluble form [17, 18]. These by-products are easily washed away. In some other cases, the template is formed in situ as a complex which decomposes with the ion consumption during the progress of the reaction [19]. Template-assisted micro and nanostructuring is also used for fabrication of superhydrophobic inorganic materials [20, 21]. Introducing thermal annealing as another step into the assisted sol-gel process resulted in much higher water contact angle of the 2D hierarchical structure replica due to heat deformation of the template, prior to the process [22]. Using inexpensive template methods, both doubly and triply scaled hydrophobic metal oxide as well as metal interfaces could be generated [21]. In contrast, embedding of desired material into the template can be achieved also by non-wetting methods. In a recent study, Ganesh et al. used sputtering at glancing angle to directly deposit a metal into the aluminium template pores [23]. This method has significant control over the morphology and distribution for the generation of nanorods of aluminium and tungsten through the template and the length of the wires depend solely on the deposition time.

2.2. Electrospinning

The process of electrospinning makes the practical use of electrostatic force to generate continuous and fine filaments from melt, sol-gel or solutions of various polymeric materials. The schematic of the process is shown in Figure 3. The main advantage of electrospinning is that it allows the addition of suitable fillers, including clay or other inorganic particles, directly into the solution to get a composite filament, while the diameter can be kept at around 10 nm [24]. Moreover, electrospinning is a low cost process and can be easily scaled up for industrial production. The surface energy and topological characteristics can be controlled by choosing the right material and suitable process parameters [24]. The material which is released from the needle tip gets deposited directly on the collector and there is no material loss during the production. Electrospinning forms nanofibres, which provide a high degree of roughness on the surface. In addition to roughness, surface tension can also be tailored by choosing the appropriate material or adding sufficient amount of additives in to the spinning solution. Appropriate combination of both effects gives superhydrophobic surface.

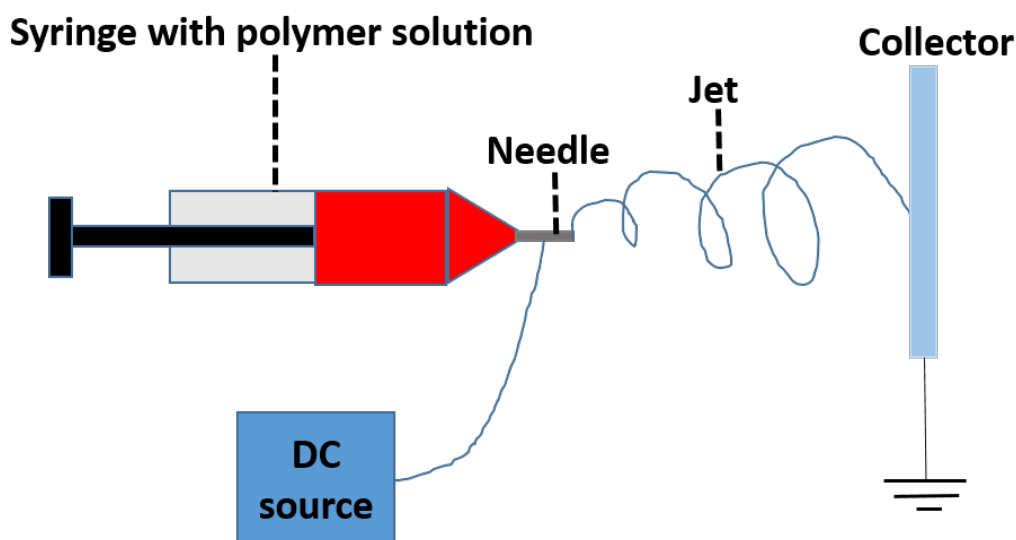


Figure 3. Schematic of the electrospinning process.

Electrospinning technique has been utilized to generate natural mimic surfaces. Lei *et al.* developed the electrospun fibres composite with porous micro particles inside, which imparted lotus leaf-like hydrophobic surface. The hierarchical structures generated by the accumulation of the fillers on the surface resembled the branch like nanostructures on the top of the micro papillae on the lotus leaf which imparted sufficient roughness to the surface to stabilise the water droplet at a contact angle above 162° [25]. On the other hand, addition of inorganic additives into the spinning solution made a nanocoating of the periphery of the fibres and increased the surface roughness. Furthermore, the time required for the trapped solvent to diffuse from the bulk of the deposited filament to its surface (drying procedure) can influence the migration of the fillers towards the outer surface of the fibres [26]. However, hydrophobic properties can be further improved by functionalising the silica before it is put

into the spinning solution. For example, epoxy-siloxane modification of silica particles causes a homogeneous self-assembly of the particles on the surface and provides better durability of the hydrophobic surface [27]. As an alternative to additives, different spinning techniques are also employed for increasing the surface energy of electrospun materials. Changing the spinning material to polymethylsilsesquioxane, the properties were not just restricted to higher water contact angle, but the difference also improved solvent resistance and thermal stability [28]. Hydrophobisation of electrospun fibres is even applicable for block copolymers. Even with 20 mL volume of water, drops exhibit contact angle values high enough to satisfy superhydrophobic behaviour on polystyrene-block-dimethylsiloxane fibres [29]. The existence of the water droplet on the spun surface and SEM images of the spun fibres are as shown in Figure 4.

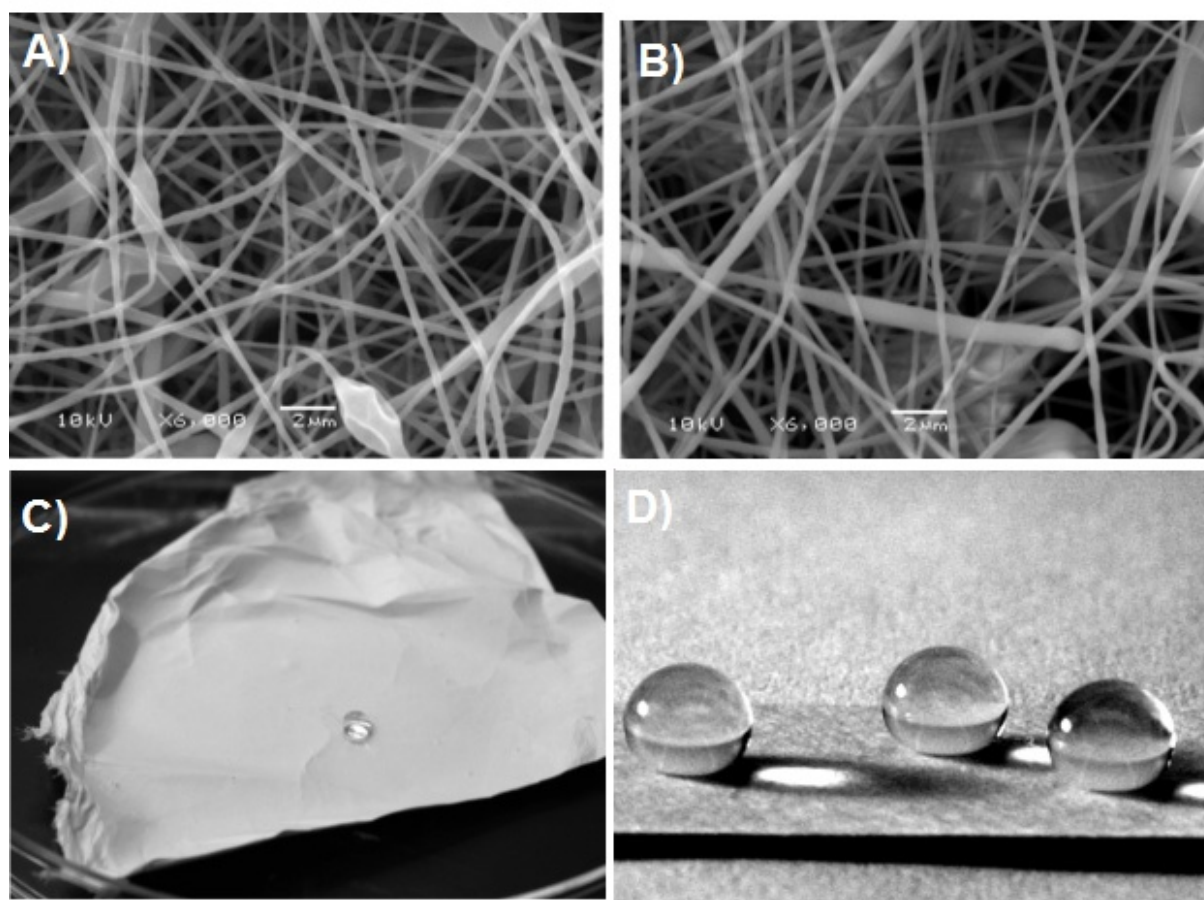


Figure 4. SEM images of electrospun fibres. (a) PS-PDMS/PS sample 6000 \times magnification (scale bar 2 μ m), (b) PS fibres 6000 \times magnification (scale bar 2 μ m), C) Free-standing mat composed of the PS-PDMS/PS electrospun fibres with a water droplet on it, D) several 20 mL water droplets on the mat, showing the superhydrophobicity. [Reproduced with the permission of American Chemical Society, *Langmuir* 2005, 21, 5549-5554]

In addition to this, various advanced techniques such as coaxial electrospinning, electrospinning with a rotating disk, needleless electrospinning, etc. are used for improving the properties of electrospun fibres [30]. For instance, recently designed multi-nozzle electrospinning set up

has an advantage to create micro sized beads from one nozzle where the other one creates fibre-like structures. The membrane maintains mechanical integrity and superhydrophobicity [31]. For further improvement in the hydrophobic character of electrospun fibres, different surface modifications are also found effective. But with many of the low energy polymeric materials, hydrophobicity can be achieved without any secondary modifications [24, 32].

Electrospinning technology is even used for fabrication of superhydrophobic inorganic surfaces. Such inorganic nanomaterials could be used in various fields including optoelectronics and sensing devices [33]. In most of the cases, precursor is created in the form of thin nanofibres of the desired oxide and hydrophobised with suitable post treatments [34]. But in certain cases, metal particles that are inserted into low energy polymers are directly used for the required applications including acid corrosion resistance [35].

2.3. Hydrothermal synthesis

Many inorganic oxides are highly insoluble in water under room temperature. The insolubility may be overcome by use of hydrothermal process which is employed with increased temperature and even pressure in certain cases. This method is very efficient in the preparation of compounds of elements in oxidation states that are difficult to obtain otherwise, synthesis of meta-stable states and varieties of crystals in high quality and good control over size and morphology [36]. Although it is widely used even in material synthesis, very high production cost and difficulty to monitor the crystal growth during the course of the process are some disadvantages.

Hydrothermal synthesis can provide hierarchical structures which can provide both hydrophilic and hydrophobic behaviour after suitable modifications. The control over the morphology is governed by the reaction time and temperature [37]. Generation of highly rough flake, flower-like or rod structures of metallic substrates are sufficient to provide enough roughness for constructing superhydrophobicity [38]. But as in the case of sol-gel synthesis, suitable surface modification is needed. Various polymeric supports, such as polyethylene glycol, are typically used for the improvement of topological properties. These supports, when adsorbed on the metal substrates, inhibit the crystal growth on certain spots and provide micro/nanoroughness to the material [39]. Hydrothermal process with only ultra-pure water as the reaction medium is a green technique and efficient in the production of complex biomimics with rough textures directly on metal surfaces. With additional hydrophobisation with suitable methods, hydrothermal process has been proven to be a great manner to protect various metals from corrosion [40, 41]. Very recent reports showed some interesting hierarchical mixed metal oxide nanoarrays, in which the hairy-like structures out of ZnO was grown on copper oxide nanowires by hydrothermal process followed by thermal oxidation as shown in Figure 5. After silylation of the surface, the contact angle went to a value of about 170°. These kinds of materials show a shift between Wenzel and Cassie state and are self-cleanable [42]. Similarly, hierarchical structured topology is applied even for the inner and outer surfaces of metallic cylinders for increasing the water repellence and thereby corrosion resistance and iceophobic properties [43, 44].

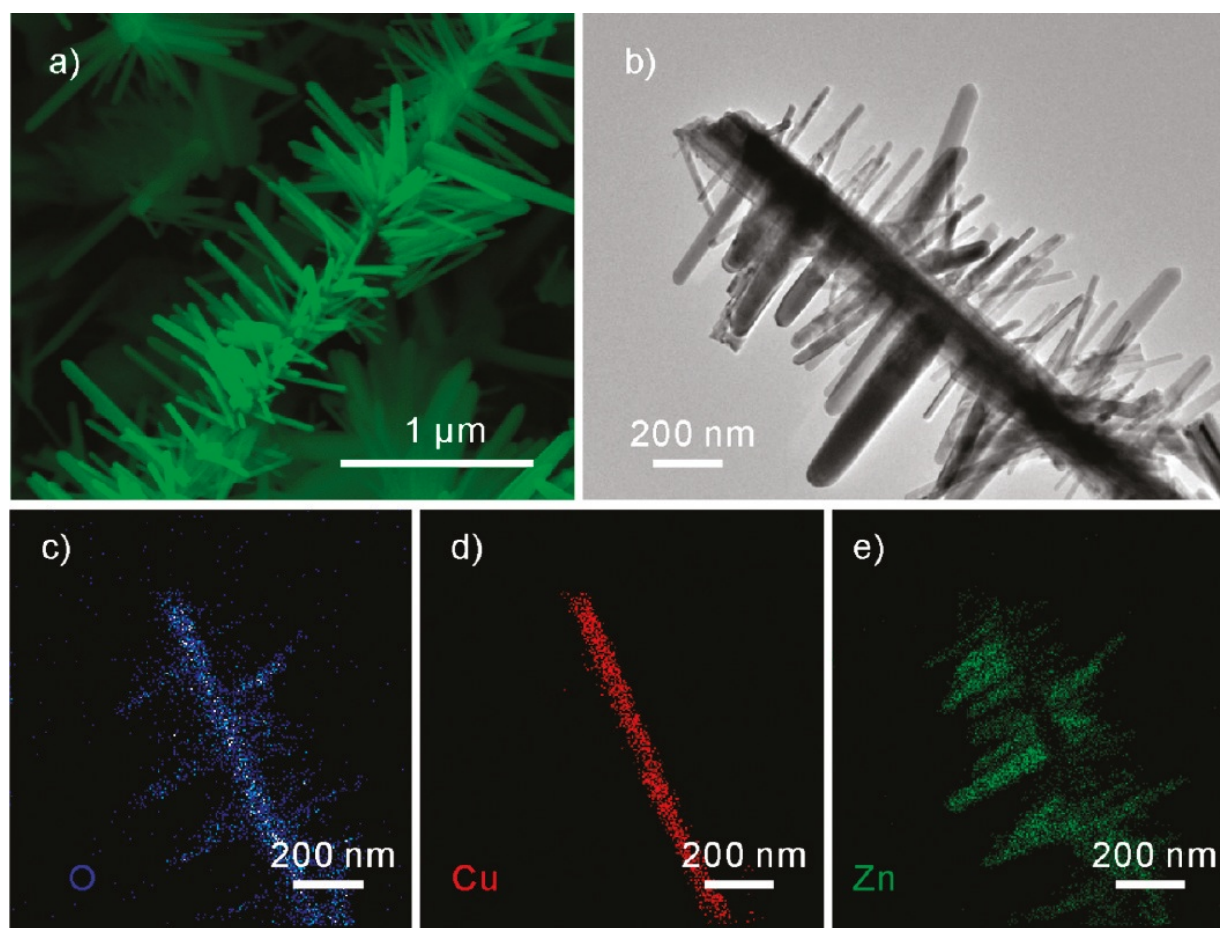


Figure 5. Component analysis of ZnO/CuO heterohierarchical nanostructure. (a) SEM image. (b) TEM image (Ni grid used here). (c-e) O, Cu and Zn elemental mapping recorded from an individual heterohierarchical nanostructure, respectively. [Reproduced with the permission of American Chemical Society, *Langmuir* 2011, 27, 6193-6200]

2.4. Sol-gel

Sol-gel method is associated with the change of the state from colloidal suspension of solid particles into a liquid dispersed in solid. During this transformation, the repelling particle interaction has been changed into attractive interaction between the particles within the colloidal state. Sol-gel processing can transmit multifunctional characteristics to the surface because of the presence of more than single functionalities in the sol state. This is typically carried out by hydrolysis and polycondensation in the presence of a suitable solvent. The solvent must have desired polarity and gets trapped inside the solid particles and forms a gel during the procedure [45]. Such gels can be easily applied on to the substrate, for example dip or spray coating with or without additives, depending on the nature of the material and the synthesised sol. The topological and chemical properties of so created surfaces largely depend on the physical properties and chemical composition of the reaction mixture. The main advantage of this method is that it is very easy to apply on to a large area of complicated structures. The hydrophobicity of composites has been improved by the incorporation or functionalization of the nanoparticles used for the processing or by various surface modifica-

tions, such as etching, to tailor the roughness [46]. Silica is one of the major nanocoatings for hydrophobisation and can be easily synthesised by sol-gel method. However, silica particles can behave as hydrophilic material because of the large amount of silanol groups on the surface. Thus, in many studies silanol groups have been functionalized with non-polar chains to induce better hydrophobicity [47]. But one disadvantage of such functionalization is that the moisture absorption can be increased with surface contamination and ageing [48]. However, metal oxides do not behave as hydrophobic surfaces without suitable functionalization in most of the cases. In case of metal oxides, functionalization could be their treatment with suitable acids and consequential surface conversion into salt, which provides improved water repellence [49].

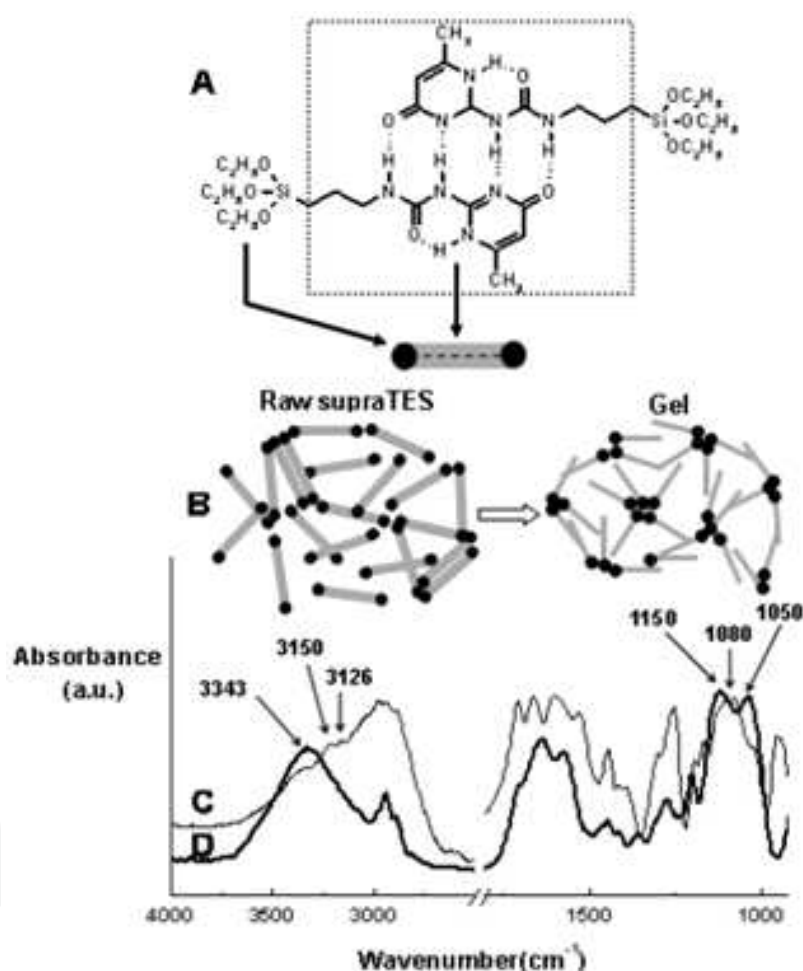


Figure 6. A) Possible structure of a synthesised supramolecular organosilane, B) Schematic of gelation with FT-IR spectrum of the corresponding formed gel. [Reproduced with the permission of American Chemical Society, *J. Am. Chem. Soc.* 2004, 126, 4796-4797]

One of the important applications of the sol-gel method in the recent years is the coating of fabrics of natural fibres with hydrophobic metal oxide colloids. This provides an open way for the fabrication of water repellent textiles for mass production. Various organosilanes and mono-carboxylic acid functionalised alumina were found very efficient [50, 51]. Such organi-

cally modified nanoparticle coating gives an additional benefit of UV blocking, and thus makes this method more interesting for textile industries [51]. Sol-gel synthesis started to utilise supramolecular assembly of long chain molecules, formed as a result of intra molecular hydrogen bonding (Figure 6) [52]. Another advantage of this method is that it is easy to conduct template-assisted sol-gel synthesis, which makes the replication much easier.

2.5. Layer by layer method

In this technique, the generation of one layer of material over the other is performed to get a multilayer composite material surface. Techniques, typically used to achieve this, include dip coating, spray coating or spin coating. The prominent application of this method is to combine the properties of various nanomaterials with polymers, which are efficiently used in biological applications [53]. Besides coating, supramolecular self-assembly can be used to generate hydrophobic surfaces. This is mostly applicable to polyelectrolyte macromolecules because of the ability of opposite charges to accumulate as layer. However, the other neutral type nanoparticles can be deposited as different layers [54]. On the other hand, charged inorganic materials along with polyelectrolytes are also employed in many cases which provide a simple route for self-assembly on various substrates and avoid the requirements for using deposition techniques [55]. Cheap scalable antifouling superhydrophobic coatings can be fabricated by introducing a lubricant into the pores of the nanostructured surface.

Layer by layer techniques are often combined with other deposition techniques for achieving higher contact angles. These deposition techniques are used for easier deposition of inorganic particles on the self-assembled macroscopic layers. Combinations of such techniques have been utilized for creating natural mimics [56]. One of the limitations for using highly charged macromolecules is that it is highly influenced by the strength of the ions present in the solution, which may result in the disassembly of the layers [57]. Such influences of the ionic concentrations can be excluded via covalent bonding of one layer over the other. Covalently bonded molecules with very long non-polar tails can thus provide water contact angle above 150° and in addition the extra stability. Other chemical interactions, such as hydrogen bonding, can also be utilized for self-assembly of layers but these are not as strong as covalent bonds. To stabilize such assemblies we need to provide additional stabilization methods such as incorporation of electrostatic copolymer with suitable multivalent ions, or suitable thermal or radiation curing of the films [58].

Recently, Huang *et al.* attempted a formation of assembled layers from colloidal dispersion by incorporating highly rough, raspberry-type particles to obtain water pinning on oleophilic surfaces [59]. Raspberry resembling films have been prepared from various micro- and nanoparticles and employed in the layer by layer assembly procedures to achieve superhydrophobicity [60]. These researchers made layer by layer method more convenient to apply irrespective of the material compared to the other commonly used techniques. This makes the method more promising for water-oil separation in industrial scale and functionalizing complex porous and membranous structures. Multilayers of strippable silver generated in lasagne-like structures took advantage of the protection from the top layer, and after modification water contact angle increased to 146° (Figures 7.1 and 7.2). Furthermore, after extreme

exposure to the corrosives, the damaged layer can be removed and a fresh layer is exposed, which gives regeneration property to the material [61].

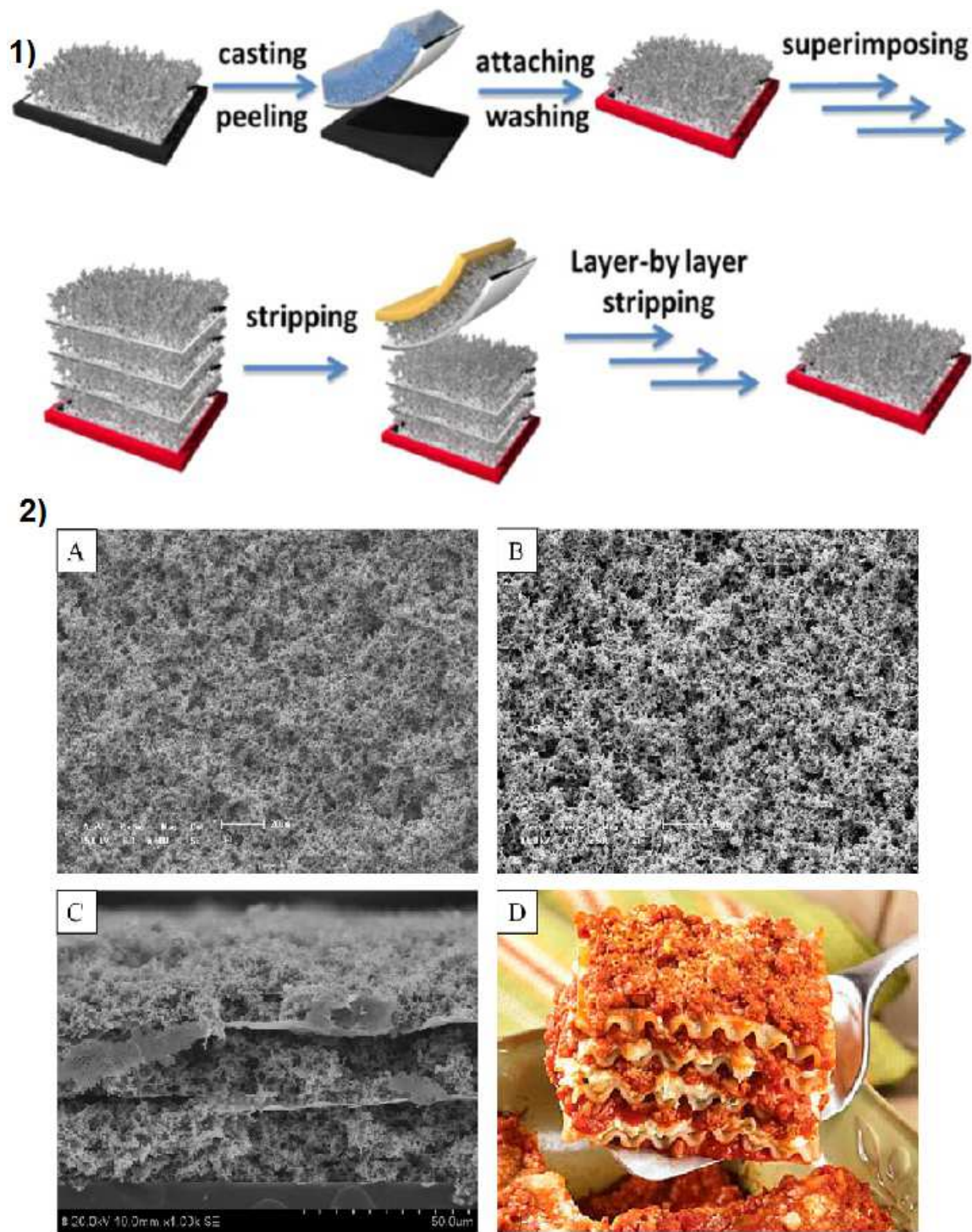


Figure 7. 1) Schematic process of fabrication and layer-by-layer stripping of the modular assembly multilayer film. 2) SEM images of the silver mirror multilayer films with three layers A), four layers (B), the cross-sectional view (C), and a photo of lasagne D). [Reproduced with the permission of American Chemical Society, *Langmuir*. 2014, 30, 548–553]

2.6. Deposition methods

2.6.1. Vapour depositions: PVD and CVD

Physical vapour deposition (PVD) and chemical vapour deposition (CVD) are the two major vapour deposition techniques used for making very thin layer of coating on various substrates. PVD utilizes the evaporated pure material whereas CVD utilizes a mixture of chemically reactive components, which are deposited on the surface, leaving the desired thin layer of coating. For the production of superhydrophobic surfaces, very low surface energy components' vapours are applied on to the surface to form a thin layer of rough and water repellent surface. For depositing such materials, various techniques including plasma, thermal evaporation or even both are used [62, 63]. Typically, plasma-assisted vaporization requires much less thermal excitation, which is a special advantage [64]. The vapour deposition coatings can be extended from inorganic metal oxides to various organic low energy materials, depending on the requirement and the substrate to be coated. Recently, surface modified silica deposition was achieved at a very low temperature of 40° C by implementing NH₃ as a catalyst into the processing chamber [65]. Developing such a low temperature processing is the best choice for coating thermally unstable surfaces. CVD has significant achievements even to control the crystallinity of the coated polymeric surfaces, tuned by controlling the deposition parameters [66]. Such control over orientation of the polymer chain deposited can significantly affect the topology of the surfaces.

Since carbon nanotubes and other graphene-related materials have excellent surface roughness and low surface energy, they are used as intrinsic hydrophobic coating, applied for water-oil separation [67]. Template-assisted vapour deposition of graphene is becoming popular for improving the porous structure with better control over the morphology, although it needs to be coated with non-polar polymer or other coatings for hydrophobisation [68]. On the other hand, carbon vapour deposited nanotubes can show superoleophilicity without any further modification [69]. Zwitter ionic deposition is another recent development for ant-fouling surfaces, where the surface energy depends on the number of exposed zwitter ions and the type of atmosphere that is exposed to the periphery, but has to be modified further to reach higher contact angle values [70].

2.7. Plasma surface treatment

Gaseous plasma is by definition partially or fully ionised gas, but it can contain also neutral gas which can be in excited state [71]. Plasma discharge can be achieved by different setups, and the reader is encouraged to read more about them [72-74]. In general, plasma particles are excited (ionised, metastabled) and even more energetic than neutral gas, and thus they can physically or chemically react with treated material. The interaction can lead to etching or deposition. Etching is achieved through physical sputtering by ions or chemical reactions with the surface and desorption (i.e. oxygen neutral atoms chemically bond to a carbon on a polymer surface and CO or CO₂ molecule is desorbed). Deposition can occur through chemical bonding of precursors from plasma to the surface or by plasma-activated chemical reactions of chemicals that are on the surface.

2.7.1. Plasma etching

Creating appropriate topography of the micro-rough surface for obtaining superhydrophobicity can be a challenge. Akinoglu *et al.* investigated plasma etching mechanism by oxygen plasma etching of polystyrene [75]. They used two setups: capacitive coupled RF low-pressure oxygen plasma (CCP) and inductively coupled RF low-pressure oxygen plasma (ICP). In both, ions and radicals and other energetically excited species contributed to the etching. Since ions are charged particles, they are directed by the electric field. The ion contribution to etching is then anisotropic, whereas the neutral species etch in isotropic manner due to diffusion governed movement. Thus, the density ratio between charged ions and neutral oxygen atoms influences the etching of the surface structure. The anisotropy in case of CPP was found to be 0.45, and in the case of ICP it was 0.21. Additionally, the etching in ICP setup was 1 order of magnitude faster than in CCP.

Despite slower etching rates, Salapare *et al.* used low-pressure CCP RF oxygen plasma for polytetrafluoroethylene (PTFE) treatment. They found a correlation between plasma power and the time of treatment with the water contact angle. With higher power (400 W) and longer time (5400 s) they managed to create super-hydrophobic surface (151° contact angle). The FT-IR and surface roughness measurements showed that only the geometrical shape contributed to the surface energy, while the chemical composition of the surface remained the same.

PTFE was treated also with a mixture of oxygen/argon magnetron plasma [76]. With plasma etching, micro-rough surface was established, and after 4h of treatment, leaf-like protrusions were created. The contact angle changed from non-treated sample at 102° to super-hydrophobic at 158° (Figure 8). The hydrophobicity was asserted to surface roughness and not surface chemistry, which was confirmed by XPS and Raman measurements.

One has to be careful when using plasma etching, because it can also damage the surface and deteriorate the hydrophobicity as demonstrated by Zylka [77]. He prepared samples from silicone rubber with surface moulded by an acrylic paint template and left them exposed to the outside weather conditions for 45 days. The water contact angle on this surface was 149° . Then he treated the samples' surface with atmospheric air corona discharge for 100 h, and the contact angle dropped to 119° .

However, superhydrophobicity can be achieved on silicon surface too. In [78] complicated plasma etching procedure was used to create nanopillar and nanocone silicon surface. The surface was additionally passivated by octadecyltrichlorosilane monolayer. In both cases super-hydrophobic surface was achieved—contact angles were 150° for nanopillars and 165° for nanocones.

Another way of obtaining superhydrophobic properties of a surface is to deposit a thin layer on it and then modify this layer's wettability. This challenge was addressed by Cai *et al.* who created polymer composites with silica spheres [79]. Then they used reactive ion etching in oxygen plasma to selectively etch the polymer and expose the silica spheres. Depending on the time of etching, different extents of the spheres were exposed. This was not sufficient for the hydrophobicity, so the liquid HF was used to etch the silica. In this manner they managed to prepare a periodic pattern of voids with the precisely selected size in the surface, and thus

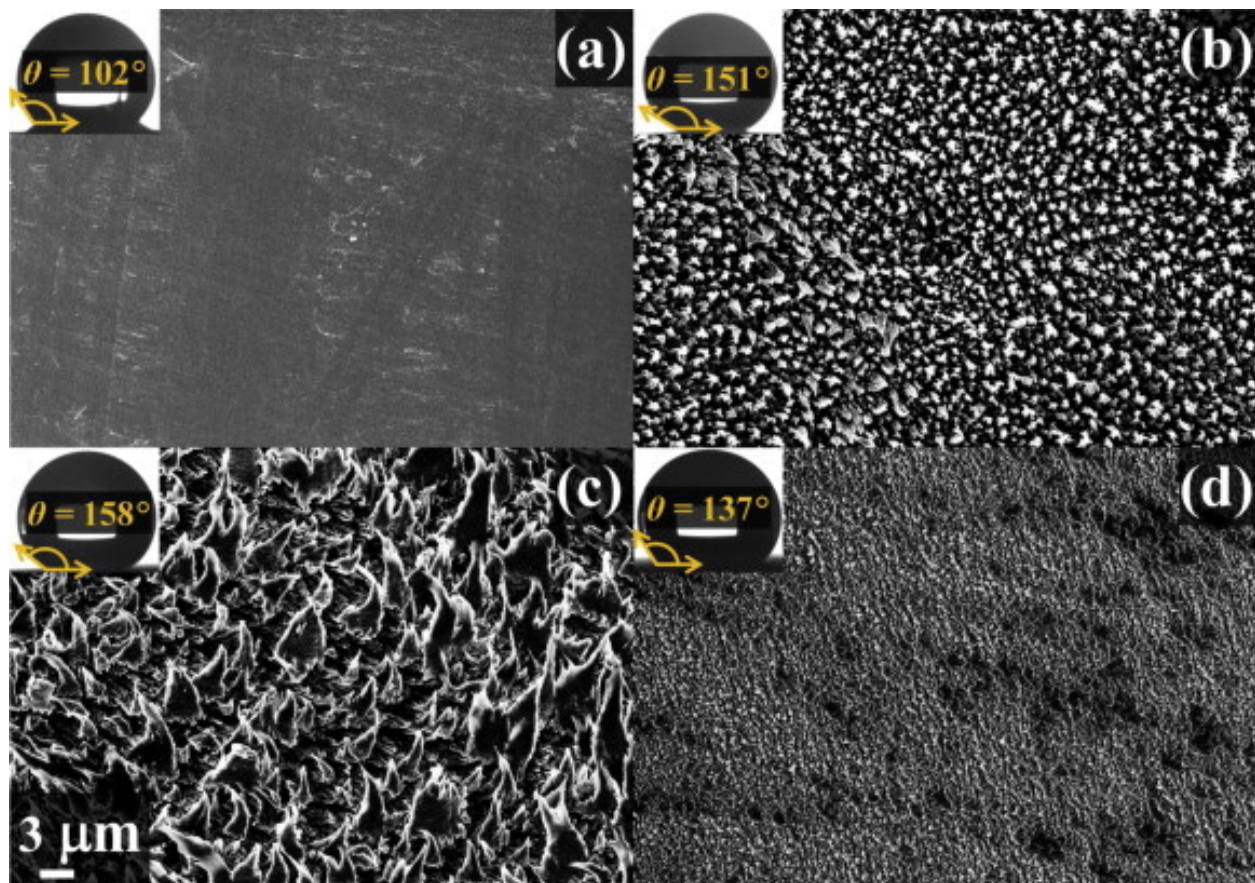


Figure 8. Insets show the FESEM surface micrographs of: (a) TF0 (untreated), (b) TF2 (2 h plasma treated), (c) TF4 (4 h plasma treated) and (d) TF5 (5 h plasma treated) PTFE samples. [Reproduced with the permission of Elsevier, *Dielectr. Electr. Insul.* 2014, 21, 1183-1188]

control the roughness necessary for the hydrophobic effect. With addition of fluorosilane the surface energy was further reduced and superhydrophobicity with contact angle of more than 150° was achieved.

2.7.2. Combination of plasma etching and deposition

To avoid many-step procedures and complicated setups, plasma etching and plasma deposition can assist in producing superhydrophobic polymer surface. Plasma etching break chemical bonds via high energy particle interaction with the surface and creates micro or nanorough surfaces by taking out the pieces of degraded polymers atom-by-atom into volatile molecules. This was nicely demonstrated for polymethyl methacrylate etched in helicon RF plasma, where etching was controlled by ion flux [80]. The ion flux was adjusted with oxygen pressure and ion energy by biasing the samples (Figure 9). The roughness was increased with lower ion flux and with higher ion energy. When bias and pressure are set, time of plasma treatment determines the RMS roughness. Additional deposition of CF_x film passivizes the surface, namely reduces the surface energy. The contact angle increases with etching time and reaches maximum value of 150° after 2 min. Similar work was performed on polystyrene, where first etching was performed with CF_4 plasma and then CF_x film was deposited by

PECVD from C_4F_8 gas [81]. In this case, CCP plasma was used. Plasma etching at 50 W was the most optimal for designing superhydrophobicity of the surface with the resulting contact angle of almost 160° . This surface property might be due to the highest fluorine-to-carbon atomic ratio on the surface after the deposition on this micro-surface structure. When the power was raised, the ion flux to the surface increased, leading to increase in the roughness and decrease in contact angle.

An interesting case is also treatment of paper (cellulose fibres) with plasma. Balu *et al.* used CCP plasma with grounded electrode for treatment as well as substrate heating to 110°C . First, the etching was carried out with low pressure O_2 plasma, followed by deposition of fluorocarbon film from pentafluoroethane-monomer [82]. The fluorocarbon film reduced the surface energy of the surface, whereas the etching increased the roughness of the fibres' surface with nanometer-scale features. This contributed to the increase in hydrophobicity, which manifested in larger contact angle (more than 160°) compared to the samples on which only fluorocarbon film was deposited (more than 130°).

Treatment	Contact angle/ $^\circ\text{C}$			
	Water		Decane m m	
	Flat	Porous	Flat	Porous
Untreated	116	146	46	Wicks
O_2 plasma	131	153	55	Wicks
Plasma polymer	131	144	83	115
O_2 plasma + Plasma polymer	148	152	92	133

Table 2. Probe liquid contact angles for flat and porous PTFE substrates [Reproduced with permission of American Chemical Society, *Langmuir*. 2007, 23, 12984-12989]

With a combination of plasma etching and deposition one can tailor the surface properties in the way that, in addition to superhydrophobicity, increased repellence of non-polar liquids is achieved at the same time. Coulson *et al.* tailored surface morphology by low pressure inductively coupled oxygen plasma, and surface chemistry by deposition and polymerisation of 1H,1H,2H,2H-heptadecafluorodecyl acrylate in the same system [83]. The substrate was either flat or porous PTFE foil. The surface microstructure exhibit hydrophobicity, and polymer prevented potential capillary effect. This increased the repellence even for decane (Table 2). In this case, Cassie-Baxter relationship seemed much better to describe the system than Wenzel's theory.

Sometimes one would need hydrophobic and hydrophilic surface on same kind of sample for different use. Ruiz *et al.* demonstrated that with the appropriate selection of polymer deposition one can tune the wettability [84]. In their work they deposited photoresist on a flat surface. Then they used inductively coupled SF_6 plasma for etching and creating micro-structured surface of the photoresist leading to the increase the fluorine-to-carbon atom ratio on the surface (Figure 9a and 9b).

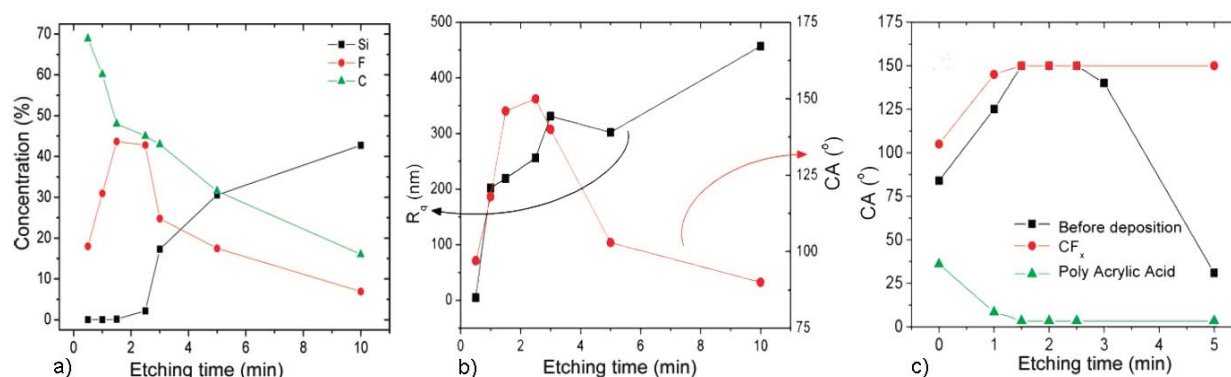


Figure 9. a) Elementary concentration obtained from XPS measurements, b) roughness and contact angles and c) contact angles with or without coatings for the SF₆ etched photoresist coated silicon surfaces. [Reproduced with permission of American Chemical Society, *Langmuir*. 2007, 23, 12984-12989]

Then they coated the etched surface with CF plasma, and afterwards they deposited polyacrylic acid (PAA) by capacitively coupled plasma. The etching already caused the superhydrophobicity, which was then slightly increased by the CF coating. However, the PAA drastically changed the surface energy and caused surface superhydrophilicity (Figure 9c).

2.8. Plasma deposition

Plasma deposition is an efficient process to deposit material with low surface energy and effectively improve hydrophobic properties. The deposited films can contribute to increase in the hydrophobicity with their structure. Most of the effects that lead to surface energy modification were already described before.

Typically, highly polar material gets deposited in a way that the surface is nanorough. Examples are atmospheric pressure plasma polymerization of the toluene/HMDSO [85], expanding plasma arc deposition of Teflon [86], pulsed CCP RF plasma deposition of fluorocarbon films from C₆F₆ monomer precursor [87] and ICP plasma deposition of perfluorooctyl acrylate film [88] that all cause the superhydrophobicity.

3. Conclusions

In this chapter various methods were introduced on how to deal with the surface energy modifications. There are three major aspects for this, either by modifying the surface morphology in the way to mimic natural structures, which are effective for water repelling (lotus effect), by functionalization of the surface by non-polar group, or deposition of material with low surface energy. It was also shown that the most successful way is a combination of the techniques—deposition of the low surface energy material on the surface and creation of its microstructure, which can additionally increase the water contact angle.

Methods such as sol gel are very simple route to achieve the high water repellence and scaling up of the process is easily achievable. Herein, many techniques for the modification of surfaces

or deposition of different low energy materials are presented, which easily lead to superhydrophobicity of surface. The future challenge has now shifted towards beneficial properties of the surfaces or the deposited thin layers like transparency, flexibility, electrical conductivity, catalytic properties, etc. without losing the superhydrophobic affiliation. Creation of antibacterial and anti-fungal surfaces for bio-medical applications are also very promising applications of such surfaces.

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