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# Superhydrophobic Surfaces: A Review

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**Abstract:**

The environmental and economic demand for oil-water separation research is attracting the attention of researchers. The oil-water separation is a challenging task in the world because of the growth of aqueous oil in polluted oceanic water, oil spill accidents, and wastewater in industrial processes such as petrochemical, daily chemical, textile, leather, and steel processing, and metal finishing every day. The wettability of water or oil on a solid surface depends on its surface chemistry and roughness. Past two decades worldwide researchers have been engaged in the fabrication of superhydrophobic and superoleophobic surfaces for oil-water separation applications. Recently, the superhydrophobic and superoleophobic membranes/sponges for the separation of oil and water have attracted increasing attention. The superhydrophobic membrane/sponge technology is the most accepted because it has low cost, is eco-friendly, has high separation efficiency, and relatively simple operational process. Polymeric membranes have unique characteristics, such as high surface area, interconnected pore structure, high porosity, easy functionality, and high-water removability. Here, we review the design, fabrication method, and recent developments of polymer/polymerized superhydrophobic and superoleophobic membranes/sponges for oil-water separation. Additionally, the effect of polymeric organosilicon and nanoparticles in composition with polymers is discussed in detail.

**Keywords**: Superhydrophobic, Superoleophobic, Superhydrophilic, Superoleophilic, Membrane, Sponge, Oil-Water separation, Hydrophobic polymers, Oily wastewater.

## 1. Introduction:

### 1.1 Wettability:

The wettability of a material refers to its hydrophilic or hydrophobic nature. The wettability of a material has a direct relationship with oxygen incorporation, which in turn affects cell adhesion. Hydrophobic surfaces show more platelet adhesion than hydrophilic surfaces. Platelets strongly attach to hydrophobic surfaces, possess spherical conformation, and therefore experience more shear stress. Even though hydrophilic substances attract platelets, those platelets get detached in a few minutes with the provision of arterial flow conditions. As the flow rate increases, more platelets detach from hydrophilic material surfaces. It is recommended to use hydrophilic material. Wettability is the character of a given material, e.g., fiber, yarn, filament, fabric, or non-woven mat, that allows liquids to adhere to its surface [1-2]. Water contact angle (WCA) is the commonly used test in laboratories to determine the wettability of materials, if WCA is smaller than 90°, the material is hydrophilic, if WCA is larger than or equal to 90°, the material is hydrophobic [3].

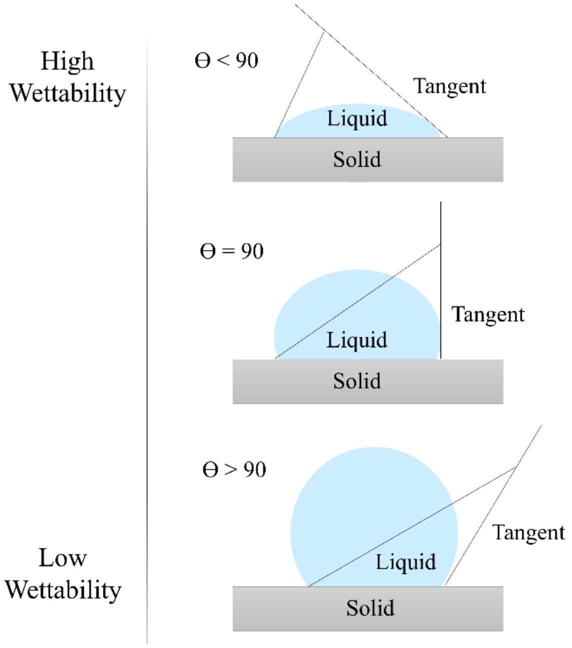

**Fig. 1. Wettability**

### 1.2 Contact Angle:

A contact angle (also referred to as a wetting angle) is formed when a drop of liquid is placed on a material surface. The surface tension of the liquid and the attraction of the liquid to the surface causes the drop to form a dome shape. If the drop is small and the surface tension of the liquid is high, it will form a perfect hemisphere. The point where the perimeter of a liquid drop, the liquid-solid interface, and the solid all meet is called the three-phase contact point. The contact angle is defined as the angle between a tangent to the liquid surface and the solid surface at this point. Theta (Θ) is the contact angle in the illustration above. If the drop of liquid spreads across a surface, the contact angle becomes smaller. If the drop of liquid beads up on the surface (as you might see with a drop of water on a water-resistant article of clothing or a waxed car), the perimeter of the drop retracts, and the contact angle becomes larger [4-5].

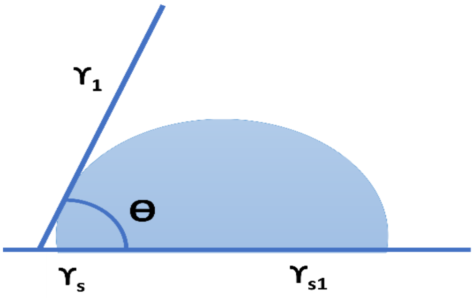

**Fig. 2. Contact Angle**

### 1.3 Hydrophilic Surface:

They are high surface energy substrates that attract water and allow wetting of the surface. They typically have a droplet contact angle measurement of less than 90 degrees. Lots of surfaces tend to be more water-friendly including, glass, steel, or stainless steel, and many coatings and paints.

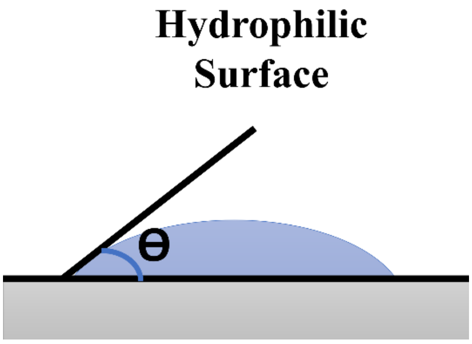

**Fig. 3. Hydrophilic Surface**

### 1.4 Hydrophobic Surface:

A hydrophobic surface is a surface that can repel water. The hydrophobic surfaces can be defined as materials that tend to repel with water. Generally, the hydrophobicity of a surface can be measured by the contact angle between the droplets of water with the surface itself. The water droplets on the hydrophobic surface will flow very easily and retain their spherical shape with a contact angle of more than 90 degrees.

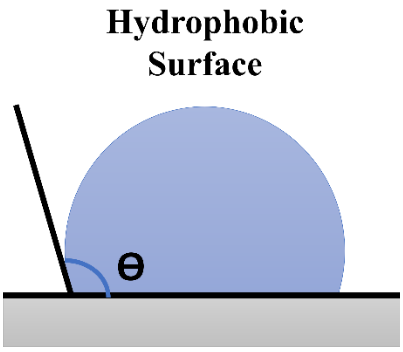

**Fig. 4. Hydrophobic Surface**

### 1.5 Superhydrophilic Surface:

Superhydrophilicity refers to the phenomenon of excess hydrophilicity, or water attraction; in superhydrophilic materials, the contact angle of water is equal to zero degrees. Superhydrophilic material has various advantages. For example, it can defog glass, and it can also enable oil spots to be swept away easily with water. Such materials are already commercialized as door mirrors for cars, coatings for buildings, self-cleaning glass, etc.

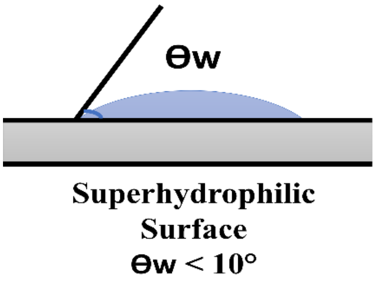

**Fig. 5. Superhydrophilic Surface**

### 1.6 Superhydrophobic Surface:

A superhydrophobic surface could efficiently reduce the contact time of bouncing drops because its contact angle is greater than 150° while the sliding angle is lower than 5°. However, the contact time of a bouncing water droplet of a certain volume on a superhydrophobic coating is constant.

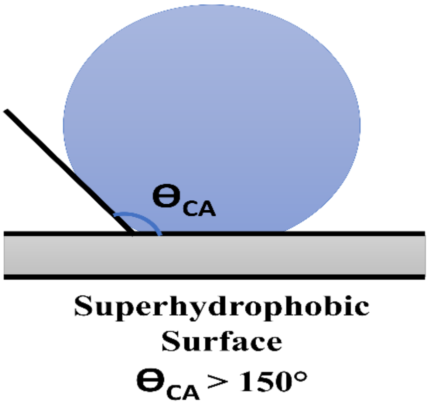

**Fig. 6. Superhydrophobic Surface**

### 1.7 Superhydrophobic Surfaces and their applications:

Superhydrophobicity and superhydrophobic surfaces have become a buzzword used to describe all kinds of surfaces with high wettability. On the internet, you can find numerous examples of coatings and materials claimed to be superhydrophobic. Some of them probably are but many are just hydrophobic. A superhydrophobic surface is defined by having a static water contact angle above 150° and a contact angle hysteresis less than 5°.

### 1.8 Superhydrophobicity was found first in nature:

The superhydrophobicity was first observed in nature on a lotus leaf and some other plant leaves that would not get wet. The term lotus effect is sometimes used to refer to self-cleaning properties that are the result of superhydrophobicity. If an electron microscopy image of a lotus leaf is taken, you would see that the surface of the lotus leaf is pretty rough. In addition, to that roughness, the surface of the leaf is covered with a wax-like material. Together, those two properties make the surface superhydrophobic [6-8].

**Fig. 8. Superhydrophobic lotus leaf**

### 1.9 Superhydrophobic surfaces require non-wetting chemistry and surface roughness:

Since the discovery of superhydrophobicity, there have been numerous examples where these types of surfaces are made artificially on various materials. As already discussed, there are two properties required for superhydrophobicity; non-wetting chemistry and micro- and/or nanostructured topography.

The non-wetting chemistry typically comes from fluoropolymer coatings. The most typical fluoropolymer, Teflon, has the highest contact angle for a smooth surface which is around 120°. It is then clear that the surface chemistry alone is not enough to make the surface superhydrophobic, but roughness is also required. The roughness requirement makes the surfaces often non-durable which is the biggest challenge in terms of their usage in different applications.

### 1.10 Applications of Superhydrophobic Surfaces:

Superhydrophobic surfaces and coatings as mentioned have a unique behavior against water droplets. This unique behavior results in a new set of applications including self-cleaning, anti-icing, antibacterial, oil-water separation, corrosion resistance, etc. Some applications are described below:

**1. Oil-water separation:**

There have been many reports of oil contaminants in sea waters and rivers due to leaks of factory waste into nature and accidents like Deep Water Horizon. Removing oil contaminants from water was always challenging and expensive; so, different methods have been introduced by scientists to remove them. These methods are categorized into three main groups: water removal, oil removal, and smart controllable separators. The water-removing filters are superhydrophilic and Superoleophobic; this kind of filter works underwater and when they get wet by water, the presence of the water on the surface of the filter prevents oil from passing from the filter pores. The category oil removing method in my personal opinion is a more efficient way because the amount of oil is always less than the amount of water; so, it is logical that we try to remove oil from water and not water from oil. To remove oil from water, the material should be superhydrophobic and superoleophilic. Superhydrophobic oil-removing filters are the main part of the oil-removing category [9].

**2. Corrosion resistance surfaces:**

There are several ways to protect a surface from corrosion. During the past two decades, scientists have been using superhydrophobic nanocomposite coatings without any toxic materials to protect various surfaces from corrosion. The corrosion protection capability of the superhydrophobic coatings mainly is because of the presence of air packets between the surface and corrosive solution, and these packets act like a barrier and prevent corrosive ions diffusion and protect the substrate [10].

Superhydrophobic metallic surfaces could be able to decrease the corrosion rate of metals by several orders of magnitude by imparting hydrophilization. Several reports have been published that demonstrated the enormous capability of superhydrophobic surfaces for corrosion mitigation. The potentiodynamic polarization test revealed a significant decrease in the corrosion current density of metallic surfaces by using a commercial hydrophobic surface modification.

**3. Self-cleaning properties:**

The lotus leaf's surface is always clean regardless of any contamination that may be present in its surrounding environment. This leaf has a unique surface structure coated with wax and shows superhydrophobic properties, and sliding angle is very low so water can easily slide on the surface of the leaf and remove any contaminants. The aforementioned properties of superhydrophobic surfaces and coatings are called self-cleaning properties. Many superhydrophobic coatings were synthesized with different methods and used in industries. It is worth mentioning that the actual self-cleaning surface is the surface exhibiting the combined super hydrophilicity and photocatalytic behaviors to decompose the dirt. The use of the term, self-cleaning surface, is not appropriate for superhydrophobic surfaces, which are extremely dry and repel water drops. These surfaces do not clean themselves but they wash away the dirt when the water drops roll over the surface [11].

**4. Anti-icing properties:**

In recent years, superhydrophobic coatings have been suggested as anti-icing coatings. As mentioned before, the presence of air packets on the superhydrophobic surfaces causes the water droplets to slide easily on the surface; therefore, there will not be enough time for the droplet to freeze on the surface;

consequently, this reduces the side effects of frosts on the surfaces. Every year ice storms harm equipment such as electrical transmission equipment, communication systems, aerospace facilities, highways, etc. To reduce this kind of damage, different methods have been developed such as local warming and preventing ice formation by chemical activities and additives, which have some limitations in practical applications. On the other hand, preventing of surface from ice development by superhydrophobicity phenomena could be practical in most cases without requiring special requirements and devices. One of the important applications of icephobic surfaces is using the insulators of transmission lines, which are needed to prevent ice formation in a cold area. The experimental survey of ice formation on coated and uncoated surfaces of an insulator under a condensing weather condition at −5°C and saturated humidity revealed that the superhydrophobic surface is completely effective in reducing ice adhesion to the surface up to 97% [12].

**5. Drag reduction:**

Drag force is one of the major problems that a solid moving in water such as a ship or submarine faces. This force results from the friction force between water and the moving solid surface in the water. Inspired by shark skin, several superhydrophobic coatings were fabricated to reduce the drag. As mentioned before, superhydrophobic coatings have some air pockets inside their hierarchical micro- and nanoscale surface structures which will reduce the contact between solid and liquid so that the drag force will dramatically reduce. The drag reduction phenomenon by superhydrophobic surfaces was investigated in various works. The superhydrophobic model ship exhibited a remarkable drag reduction of 38.5%. On a non-coated sample, the friction is just between solid and water, but on a superhydrophobic surface, there are three phases, water, solid, and trapped air between these two; so, the friction will be drastically reduced in this situation which is known as the plastron effect [13].

**6. Antibacterial properties:**

Antibacterial properties are essential in biosensors, implants, food packaging, and industrial and marine equipment. For example, one of the main reasons that cause infection in patients after surgery is bacteria that grow on implants. To solve this problem, antibacterial coatings that reduce the bacterial adhesion to the surface suitable are used. One research in this regard fabricated the silver nanoparticles on cotton fibers and then modified the hexadecyltrimethoxysilane to get superhydrophobicity. Antibacterial activity of the samples (inhibition zone formed on agar medium) has been determined. The results showed that the normal cotton samples, exhibit no antibacterial activity, whereas the silver-modified cotton surfaces killed all the bacteria under and around them showing a distinct inhibition zone with an average width of 8.78 mm around the samples [14].

## 2. METHODOLOGY

### 2.1 Sol-gel process

The sol-gel process is a bottom-up synthesis method. In this process, the final products are formed by performing several irreversible chemical reactions. This paper investigated the selection of suitable catalysts, the operating mechanism of the catalysts, and the drying steps of the wet gel. It was said that the reaction rate between water and alkoxides is very low. With the addition of alcohol, the solution becomes more dilute and the reaction rate decreases sharply. Therefore, to increase the reaction rate in the sol-gel process, a catalyst is used. It was emphasized that the catalysts used in the sol-gel process should be selected in such a way that they can be easily removed from the environment after the reaction. As a comprehensive example, the mechanism of action of acidic and alkaline catalysts in the silica gel sol-gel process was investigated. It has been said that the use of acidic or alkaline catalysts increases the rate of the hydrolysis reaction and the amount of sol produced. It was emphasized that since the solvent is one of the internal components of the gel and is responsible for forming its network, it is very difficult to maintain the structure of the cavities by removing the solvent. To maintain the integrity of the gel structure, it is necessary to allow some time before drying for the bonds between the particles to become stronger and stronger. Two methods for solvent separation from gels were introduced. In the first method, the gel is placed in the atmosphere after production to dry spontaneously [15-16]. The gel obtained from this method is called xerogel. In the second method, called the supercritical method, the changes in the solid network are minimized. The material obtained from this method has porous networks and low strength and is "hollow" in correction. This product is called aerogel. Finally, based on what has been said, it is possible to control the final structure and properties of the products obtained from the sol-gel process by precisely controlling the variables related to wet gel drying, sol, and gel synthesis.

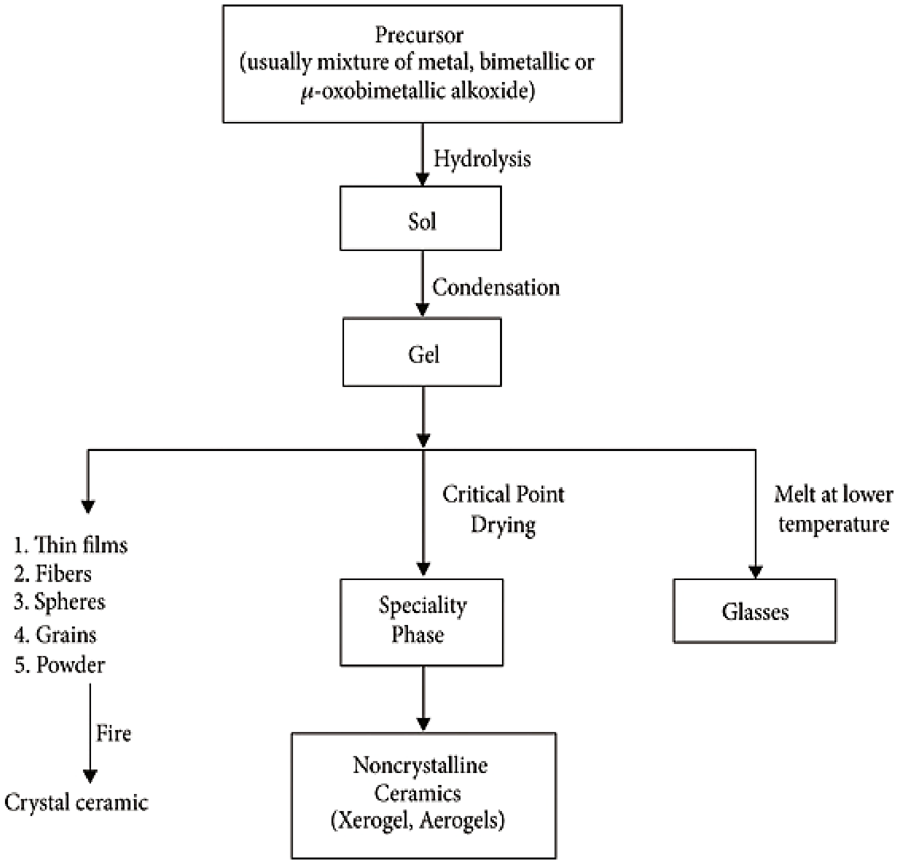

**Fig. 9. An overview of the various stages of the sol-gel process.**

### 2.2 Dip coating process:

Dip coating is a process by which substrate material is submerged in conformal coating, then taken out and allowed to drip dry. Once the excess coating has drained, the substrate material is further dried using one of a variety of techniques, often baking.

There are three essential parts in the dip coating process:

1. **Immersion:** Immersion is the first step and is exactly what it sounds like: immersing the substrate material in the conformal coating. During this stage, it's important to maintain steady speeds and smooth, unshaken conditions.
2. **Dip time:** Dip time refers to the time the substrate material remains immersed in the coating. Limiting movement is especially important during this step, or coating could become uneven and unreliable.
3. **Removal:** Removal is the final step, and, in many ways, the most important one: faster removal will result in a thicker coating, so it's important to time things carefully.

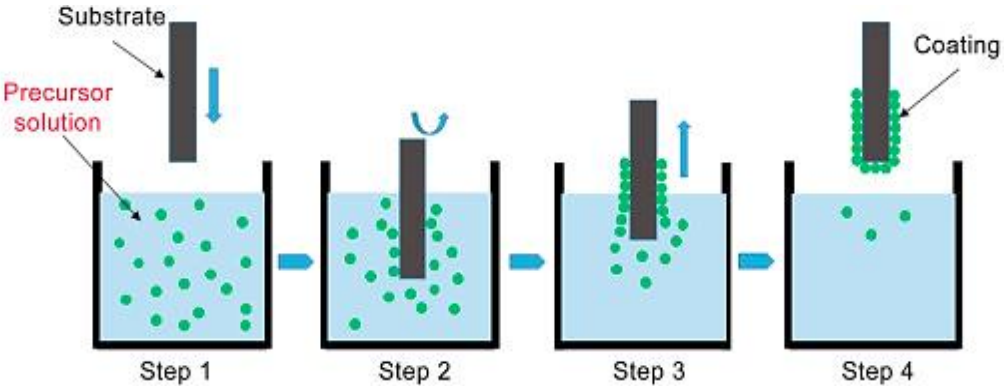

**Fig. 10. An overview of the various steps of the Dip coating process.**

### 2.3 Spray Coating Process:

Spray coating is a technique in which the printing ink is forced through a nozzle whereby a fine aerosol will be formed. In a spray coating process, the characteristic performance of polymer solar cells is limited by some drawbacks such as isolated droplets, non-uniform surfaces, and pinholes. There are a few process parameters for the spray coating that have been extensively studied such as distance between sample and airbrush, flow rate, pressure, substrate temperature, concentration of the blend solution, spray duration, cosolvent mixture, and number of times the substrate is sprayed.

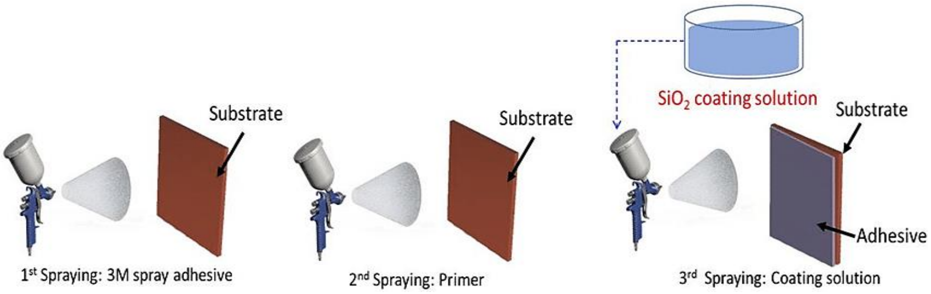

**Fig. 11. An overview of the various steps of the Spray coating process.**

## 3. CHARACTERIZATION TECHNIQUES

### 3.1 Scanning Electron Microscopy (SEM)

SEM stands for scanning electron microscope. It is a microscope that uses electrons instead of light to form an image. Since their development in the early 1950s, scanning electron microscopes have developed new areas of study in the medical and physical science communities. The SEM has allowed researchers to examine a much wider variety of specimens.

The scanning electron microscope has many advantages over traditional microscopes. The SEM has a large depth of field, which allows more of a specimen to be in focus at one time. The SEM also has a much higher resolution, so closely spaced specimens can be magnified at much higher levels. Because the SEM uses electromagnets rather than lenses, the researcher has much more control over the degree of magnification. All of these advantages, as well as the actual strikingly clear images, make the scanning electron microscope one of the most useful instruments in research today.

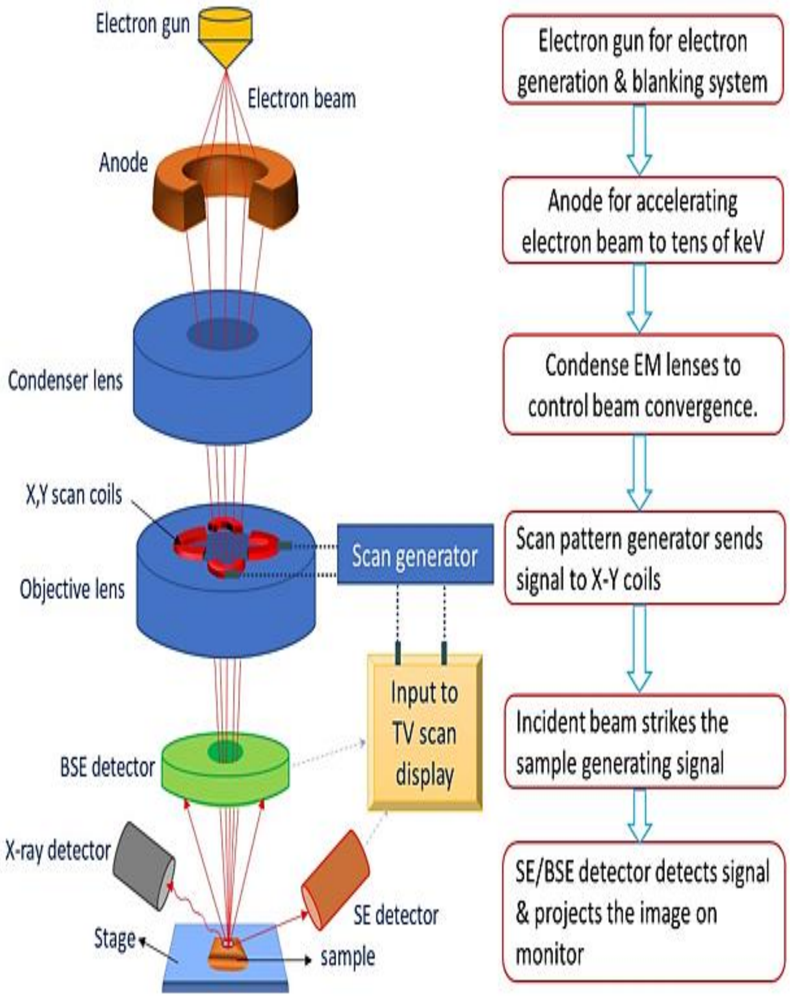

**Fig. 12. Schematic of instrumentation of SEM.**

**3.2 FTIR:**

FTIR stands for “Fourier transform infrared” and it is the most common form of infrared spectroscopy. All infrared spectroscopies act on the principle that when infrared (IR) radiation passes through a sample, some of the radiation is absorbed. The radiation that passes through the sample is recorded. Because different molecules with their different structures produce different spectra, the spectra can be used to identify and distinguish among molecules. In this way, the spectra are like people’s fingerprints or DNA: virtually unique.

FTIR is the preferred method of infrared spectroscopy for several reasons. First, it does not destroy the sample. Second, it is significantly faster than older techniques. Third, it is much more sensitive and precise. These benefits of FTIR derive from the use of an interferometer, which is the infrared “source” that allows for greater speed, and the Fourier transform. The Fourier transform is a mathematical function that takes apart waves and returns the frequency of the wave based on time. The “output” of the interferometer is not the spectroscopy spectrum we use, but a graph known as an “interferogram.” The Fourier transform converts the interferogram into the infrared spectroscopy spectrum graph we recognize and use.

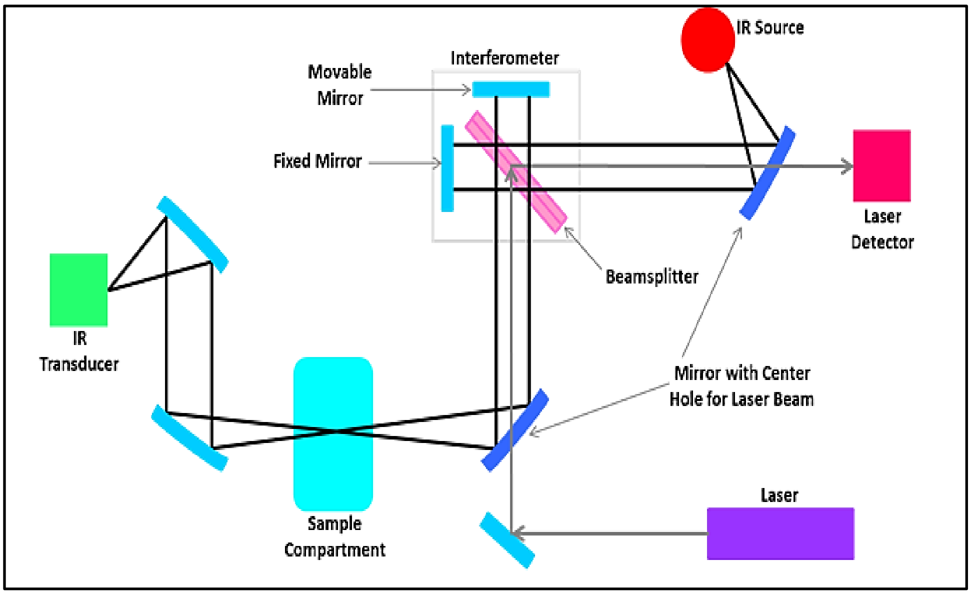

**Fig. 13. Schematic of instrumentation of FTIR.**

### 3.3 EDAX:

Energy-dispersive X-ray spectroscopy (EDS, EDX, EDXS, or XEDS), sometimes called energy dispersive X-ray analysis (EDXA or EDAX) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum (which is the main principle of spectroscopy). The peak positions are predicted by Moseley's law with accuracy much better than the experimental resolution of a typical EDX instrument.

To stimulate the emission of characteristic X-rays from a specimen a beam of electrons is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron-hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower-energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS allows the elemental composition of the specimen to be measured.

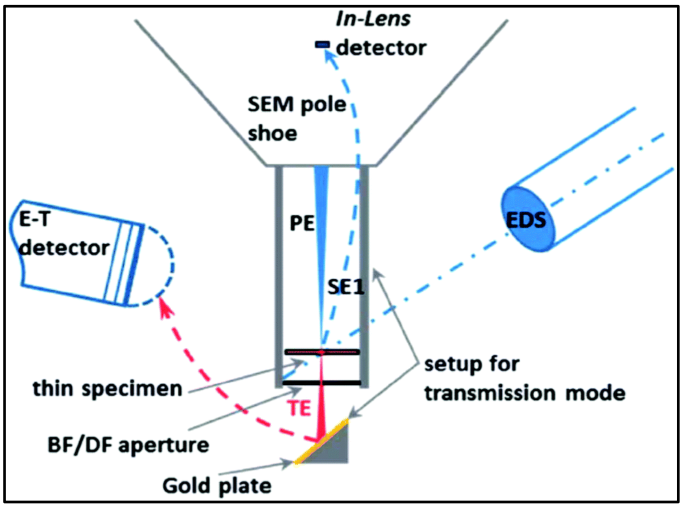

Fig. 14. Schematic of instrumentation of EDAX.

### 3.4 Contact Angle Meter:

Contact Angle Meters are used for the determination of wetting characteristics of solid materials. Contact angle meters (also known as optical tensiometers or goniometers) allow direct measurements of surface tension, interfacial tension, and contact angles. The contact angle is an extremely versatile technique used for the characterization of both liquids and solids.

The Contact Angle Meter (optical tensiometer) is an ideal industrial or academic tool for product development engineers and R&D engineers who need precision and repeatability. Contact angle measurement combines high-technology test instrumentation and a non-destructive testing method to allow an accurate, objective, and repeatable analysis to be made. Using the contact angle meter, you can compare the effects of a range of surface treatments and gather data that correlates to various surface conditions e.g., lubricity, wettability, surface energy, etc.

The equipment captures drop images and automatically analyses the drop shape as a function of time. The drop shape is a function of the surface tension of liquid, gravity, and the density difference between the sample liquid and the surrounding medium. On a solid the liquid forms a drop with a contact angle that also depends on the solid's surface free energy. The captured image is analyzed with a drop profile fitting method to determine contact angle and surface tension.

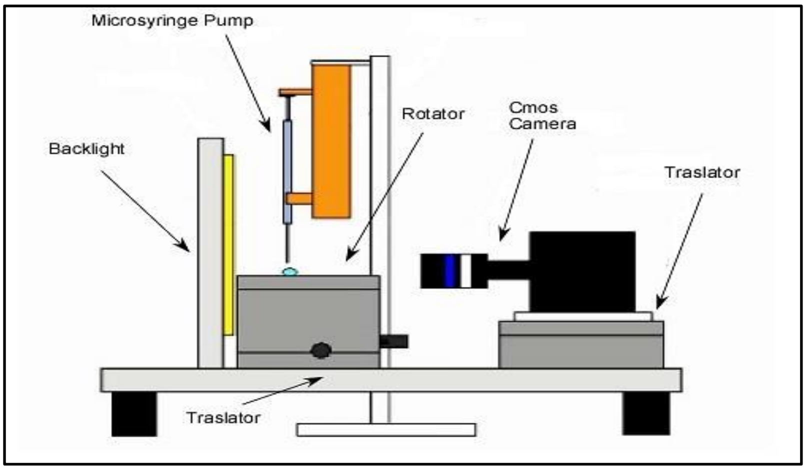

Fig. 15. Schematic of instrumentation of Contact angle meter.

## Conclusion

Natural-inspired superhydrophobic surfaces (like the lotus effect) have great promise for several uses, including corrosion resistance, self-cleaning, anti-icing, and drag reduction. The combination of low surface energy coatings and micro/nanostructures makes these surfaces extremely water-resistant. Notwithstanding its benefits, issues with sustainability, durability, and large-scale production still exist. To increase real-world application, current research is concentrated on improving mechanical robustness, scalability, and environmentally friendly production techniques. More sophisticated coatings for industrial, medicinal, and environmental uses may result from future advancements in superhydrophobic technology, making these surfaces more useful and affordable.

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