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Review Article

An overview of superhydrophobic ceramic membrane surface modification for oil-water separation



Jamilu Usman ^{a,b}, Mohd Hafiz Dzarfan Othman ^{a,*}, Ahmad Fauzi Ismail ^a, Mukhlis A. Rahman ^a, Juhana Jaafar ^a, Yusuf Olabode Raji ^{a,c}, Afeez O. Gbadamosi ^d, Tijjani Hassan El Badawy ^a, Khairul Anwar Mohamad Said ^a

^a Advanced Membrane Technology Research Centre (AMTEC), School of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

^b Department of Chemistry, Faculty of Science, Sokoto State University, P.M.B. 2134, Sokoto, Sokoto State, Nigeria

^c Department of Chemical Engineering, Abubakar Tafawa Balewa University (ATBU), 0248, Bauchi, Nigeria

^d Department of Chemical and Petroleum Engineering, College of Engineering, Afe Babalola University, PMB 5454, Ado-Ekiti, Nigeria

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ABSTRACT

The discharge of oily wastewater and offshore oil spills contaminates the biotic and aquatic environment and ultimately result in the destruction of the ecosystem. Recently, the application of ceramic membranes has gained prodigious attention due to its efficiency in oil-water separation process. Ceramic membranes developed from inorganic materials are considered as the most promising technology for the treatment of industrial wastewater. Besides, different types superhydrophobic-superoleophilic substrates are being developed using various substrate materials to tailor its purpose for higher efficiency. Nonetheless, fouling and clogging phenomena restrict the performance of ceramic membrane in oil-water separation. This review emphasizes the recent innovation on superhydrophobic methods for the modification of ceramic membranes for oil-water recovery. It comprises of an overview of the preparation technique of ceramic membrane using various techniques. Moreover, the different types of hydrophobic ceramic membrane modification using chemical agents and consequent effects on oil-water separation were discussed in detail. Furthermore, the technical challenges and issues associated with the applications of superhydrophobic-superoleophilic ceramic membrane for oil-water separation were discussed. Finally, future direction in the research of cost-efficient approach to produce superhydrophobic ceramic membranes for oil-water filtration process is enumerated.

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* Corresponding author.

E-mail address: hafiz@petroleum.utm.my (M.H.D. Othman).

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1. Introduction

A considerable amount of oily wastewater is produced and discharged daily due to the development of different industrial processes which includes; petroleum refining, food, textile, steel, and aluminium industries [1–5]. Unfortunately, the oily wastewater from these industrial processes ranks among the most common pollutants that severely contaminate the environment, thereby, causing significant adverse effects on health, environment and climate change around the globe [6,7]. To ensure a safe environment, safe regulations estimate the allowable concentration of oily wastewater from industrial activities falls between the range of 50–1000 mg/L while the allowable limit of total grease and oil concentrations in water bodies is between 10 and 15 mg/L [8–11]. Due to stricter regulations concerning the concentration of oil-water emulsion, the oily wastewater needs to be treated before discharge to the environment. Hence, oil-water separation has become a required field of research for scientific, economic, social and also environmental studies [12–16].

Hitherto, conventional separation processes such as gravity separation, skimming, coagulation, de-emulsification, oil-absorbing, coalescence dissolved air flotation, biodegradation, sonication, flocculation adsorption, and ion exchange were used for oil-water separation process [17–19]. Nonetheless, the drawback of the conventional methods includes high energy cost, ample space for installation, sophisticated separation equipment, use of toxic compounds for operation, low separation efficiencies for low concentration of oil, and generation of secondary pollutants [20–22]. Thus, the separation of oil-water emulsion requires further separation methods to

be devised in order to meet regulations concerning the oily wastewater effluent standards [23].

Recently, membrane separation processes such as ultra-filtration (UF) and microfiltration (MF) processes has emerged as an effective and efficient method for the processing of oil-water emulsion with different level of oil concentration. This method offers many advantages over conventional methods that include firmness, low cost, high emulsion separation efficiency, no phase change, no addition of chemicals and simplicity of operation [8]. Hence, this innovative technology has attracted many interests due to continuous research and development in both the academic arena and industries for the separation of oil-water emulsion [9,14,20].

Several types of membranes developed for the treatment of oil-wastewater are polymeric membrane, and ceramic membrane. Polymeric membrane separation technology has substantially addressed a wide range of applications in both scientific research and various commercial applications. Nonetheless, ceramic membranes have many advantages such as chemical and thermal stability, excellent resistance to fouling, pressure resistance, long lifetime, ease of cleaning and mechanical stability as compared to polymeric membranes [24]. Hence, the recent renewed interest towards the development and application of ceramic membrane for separation of oil-water emulsion [25–27].

As the oil-water separation has become a fundamental issue of interest, a novel approach that utilises a unique wettability of material for separation of the oil-water emulsion has been devised [2,3,28]. Recently, the materials used for oil-water emulsion separation has gained enormous interest due to their broad level of applications in various industries [29–31]. More recently, research and development have

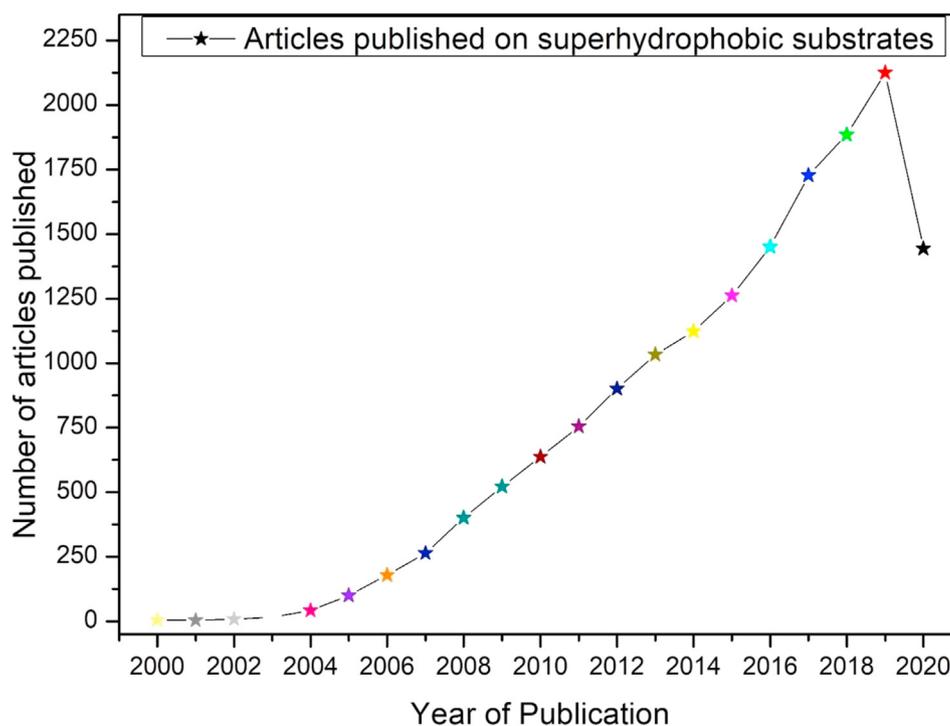


Fig. 1 – Statistical publications indexed in the web of science (ISI) by using the term “superhydrophobic”. The number of publications from 2000 to 2020.

focused on the development of ceramic membranes from benign, naturally abundant, and cost-effective materials such as kaolin [32–34], natural clay [35–37], waste material such rice husk ash [38], fly ash [39], corn cob ash [40] and palm oil fuel ash (POFA) [41]. These materials are beneficial in two ways. Firstly, they have been demonstrated to be efficient to treat oil-water emulsion at low cost. Lastly, they can effectively replace the expensive ceramic membrane raw material [42,43].

Either microfiltration or ultrafiltration method can be used in treating of oil-water separation using the ceramic hollow fiber membrane [16]. However, the membrane performance is easily compromised by clogging of the membrane pore and fouling of the surface by the oil, leading to a reduction in fluid flux. Addressing this issue will require a surface with unique wettability properties like superhydrophobic and superoleophilic which are reported to be interestingly suitable for oil-water emulsion separation [44]. Superhydrophobic surface is typically used to describe substrate material with water contact angle above 150° and low sliding angle or low contact angle hysteresis. In the past decade, research on the superhydrophobic porous substrate has been receiving much attention in various fields of academia. By mere searching the term “superhydrophobic” in the ISI web of science, until September 2020, more than 2200 records were found which indicates an accelerated increase in the number of publications (Fig. 1). This kind of surface can be realized by surface modification to improve substrate anti-fouling performance as well as anti-clogging of the pore [45,46].

Wang et al. [47], fabricated hydrophobic B-sialon planar ceramic membrane by coating with a uniform polydimethylsiloxane layer via a poly-condensation reaction. Higher contact angle of above 140° was achieved which was reported to be attributed due to the presence of Si-CH_3 groups. The same author reported another similar hydrophobic membrane developed using a porous Si_3N_4 substrate which was coated with vesicular SiNCO nano-particles [48]. Dong et al. [16] fabricated a porous SiOC superhydrophobic ceramic membranes using polydimethylsiloxane. Narrow pore size distribution of $0.83 \mu\text{m}$ for the oil in water emulsion was effectively separated with over 95% rejection rate. Abadikhah and co-workers developed a silicon nitride hollow fiber membrane for treatment of oil-field produced water. The membranes successfully treated highly concentrated (21,000 ppm) oil-field-produced-water, and an oil rejection of 95% as well as a stable permeate flux of $480 \text{ Lm}^{-2} \text{ h}^{-1}$ were achieved.

There are literature review available concerning the fabrication processes of ceramic membrane as stand-alone [32]. Besides, there are other reviews that focuses on advances on only one surface modifier as well as its fabrication process such as superoleophobic surfaces [49], superhydrophilic surfaces [50,51], superamphiphobic surface [52] and superhydrophobic surface [53,54] as stand-alone reviews, however, to the best of our knowledge there is no review article universally that discusses on the fabrication and superhydrophobic/superoleophilic surface modification of ceramic membrane for separation of oil-water as stand-alone. Herein, a mini review of the recent advances in fabrication and surface modification of ceramic membranes for the development

of superhydrophobic/superoleophilic surfaces for separation of oil-water has been presented. Superhydrophobic/superoleophilic surface is typically referred to as water-blocking surfaces that can entirely repel water while enabling the oil phase to pass through or be readily adsorbed, hence attaining an excellent efficiency and selectivity separation of water and oil. These surfaces are created by increasing the surface roughness and lowering the surface energy chemical composition by deposition [55,56].

This overview gives a better insight into different fabrication and surface modification methods for the ceramic membrane as possible solutions in tackling issues related to membrane fouling and clogging. Besides, it complements the effort of scientific researchers who study and report a significant surge in surface re-engineering as well as ceramic membrane fabrication techniques for oil and water separation. The first section of the review paper begins with a brief introduction to ceramic, oil-water issues and overview of oil-water separation using other separation techniques. Subsequently, membrane separation technology, ceramic membrane fabrication processes from different materials, separation of oil-water via the ceramic membrane, and characteristics of the ceramic membrane were enumerated in detail. Furthermore, the various available techniques used in fabricating hydrophobic ceramic membranes while the fourth section discussed applications of superhydrophobic ceramic membrane for the treatment of oily wastewater. Finally, the study was concluded by summarizing the optimum and viable method of ceramic membrane fabrication, surface modification technique for oil-water separation, challenges, and future outlook.

2. Membrane separation technology

Membranes are selective barriers between two phases where one or more species are driven by pressure/concentration/temperature differences. Membrane technology has nowadays become famous as well as accessible separation technology due to its productive separation efficiency for oil-water separation [57–60]. This is because it possesses several desired characteristics for oil-water treatment, such as pore size estimation for the molecular weight cut off; the direct pressure-driven separation between oil and water does not also require phase change for the separation to take place. These features make the utilization of membrane separation techniques to spread over and to become an essential separation technology in the world. In addition to its desired characteristics, membrane technologies also have many unique properties as well as advantages over other separation techniques such as no chemical addition, simple operation, high efficiency, time-saving, stable performance, low energy requirement, and well-arranged process conduction [61].

Generally, membrane separation technology processes are classified into microfiltration, ultrafiltration, nanofiltration, and reverse osmosis processes; the classification is based on their pressure difference which is referred to as the driving force of each process. While dialysis and membrane contactors are a classification of the concentration driven membrane, the classification is based on the concentration of the

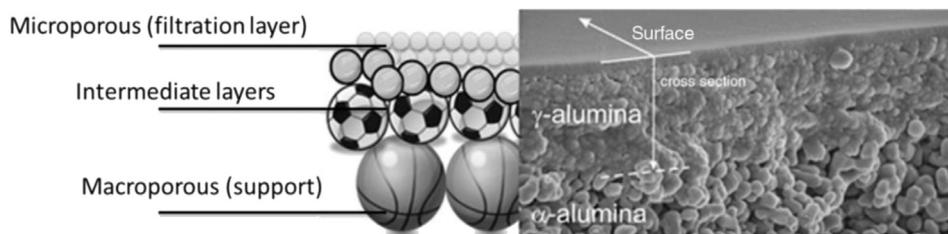


Fig. 2 – Ceramic membrane structural illustration [1].

species [62]. Membrane process-driven by a potential electrical difference is classified as an electrodialysis membrane. In general, the membrane process is classified based on the significant variations in the particle sizes of the species as the membrane pore size is almost similar to that of the sizes of the species separated [20]. In this regard, the driving forces (e.g., pressure difference) across the membrane could be lower or higher. For example, the applied pressure for the micro-filtration process is between 0.1 and 2 bar which could be increased to 5–20 bar, for nano-filtration, 10–100 bar for reverse osmosis and ultrafiltration 2–7 bar. In summary, microfiltration membranes are used for larger pore size separation while ultrafiltration and reverse osmosis membranes are used for moderate and smaller pore sizes, respectively.

The synthetic membranes are sub-divided into inorganic membranes such as ceramic membranes and organic such as polymeric membrane [63,64]. The polymeric membranes are divided into the glassy polymer; gives high selectivity but low permeation and rubbery polymers: gives high permeation but low selectivity, hence exhibit different properties in the separation process [65]. The polymeric membrane that is mostly used today around the world are fabricated from cellulose acetate, polysulfone (PSF), polycarbonate (PC), polyimide (PI) and polyethersulfone (PES). Amongst these polymers, PI received the most extensive study due to its excellent thermal, chemical and mechanical stability [66]. Hitherto, one of the drawbacks of the polymeric membrane is the selectivity permeates trade-off, which severely limits its performance. On the other hand, inorganic membrane offers superb properties compared with polymeric membrane regarding mechanical, chemical, and thermal stability. Some of the examples of the inorganic membrane are silica, titania, alumina, clays, zirconia, zeolite, kaolin, quartz, and so on.

The ceramic membrane, classified as an inorganic membrane, is described to be a permselective barrier that possesses two distinct permeability and separation factors as the performance indicators of the membrane [62]. Generally, the ceramic membrane is classified into porous ceramic membranes, which are typically governed by; surface porosity, pore size, and thickness of the membranes, and the dense ceramic

membrane, which have complex permeation and separation principles. The application and separation mechanism of porous ceramic membranes corresponds to the ceramic membrane pore size.

Ceramic membranes are also referred to as composite membranes as they consist of numerous layers of one or more distinct ceramic material. They generally have microporous support, a microporous (or a dense) top layer, and one or two mesoporous intermediate layers. Commonly used materials for the preparation of ceramic membranes are Al_2O_3 , SiO_2 , TiO_2 , etc. or a combination of these materials. After the first invention of porous ceramic membrane in 1966 [67,68], it continues to receive intensive attention towards membrane-based pressure-driven that is widely applied in micro-filtration (MF) and ultrafiltration (UF) [7,20], and recently, nanofiltration (NF) [69,70] by inducing nanoparticles on the top layers of the porous ceramic membrane. Ceramic membrane exhibits significant advantages such as the ability to withstand high temperature, chemicals, pH, etc [24,71] as compared to its polymeric counterparts. Because of their outstanding abilities, ceramic membranes are nowadays being applied as a membrane-based thermally driven channel (i.e. membrane distillation).

2.1. Characteristics of ceramic membranes

The ceramic membrane is said to be asymmetrically layered composites composed of aluminium oxide. The ceramic membrane is made of three layers, as depicted in Fig. 2; the layers comprise of; firstly, the dense layer called also the active layer or microporous that has the smallest pores and thickness sizes of about 5–10 μm . It is the innermost layer of the ceramic membrane with a porosity range from 30 to 50%, and it is responsible for the separation processes. Secondly, the intermediate layer that has a thickness of about 30–45 μm and porosity of approximately 40%. It is responsible for supporting and protecting the macroporous. The third layer is called the macroporous layer which offers mechanical strength to the ceramic membrane. It has a thickness of about 1.5–2 mm and a porosity of 40–45%. Table 1 summarised the

Table 1 – Features of ceramic-based membrane filtration [67].

Layers	Pore sizes (nm)	Mechanism	Membrane Applications
Macroporous	>50	Sieve	Microfiltration and Ultrafiltration
Mesopore	2–50	Knudsen diffusion	Nanofiltration, Ultrafiltration, Gas separation
Microporous	<2	Microporous diffusion	Gas separation
Dense	–	Diffusion	Reaction and gas separation process

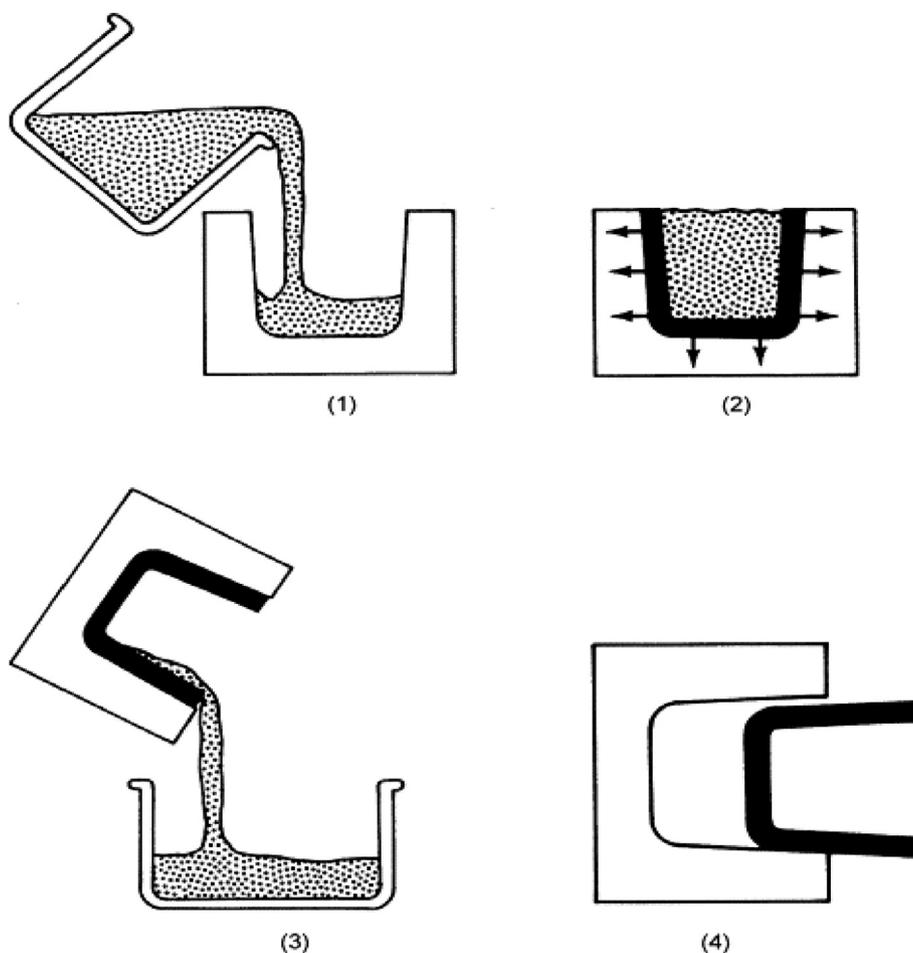


Fig. 3 – Schematic illustration of slip casting [2].

characteristic features of the ceramic membrane in terms of mode of separation, application, pore size and layer type.

2.2. *Methods of fabrication of ceramic membrane*

Ceramic membrane fabrication comprises of several methods that include solid-state, slip-casting technique, tape casting technique, pressing technique, and extrusion technique. The slip-casting technique is one of the most frequently used

methods in assembling a complex shape ceramic membrane that possesses an irregular shape and non-concentric. This method involves suspended ceramic particles in the water, which are merged into the porous plaster mould [72]. The ceramic membrane made from slip casting method is carried out by firstly preparing the ceramic suspension (mixture of ceramic solvent and powders); secondly, the suspension is then transfer into a porous mould; in there, the solvent will be diffuse via the mould pore resulting to a gel layer on the

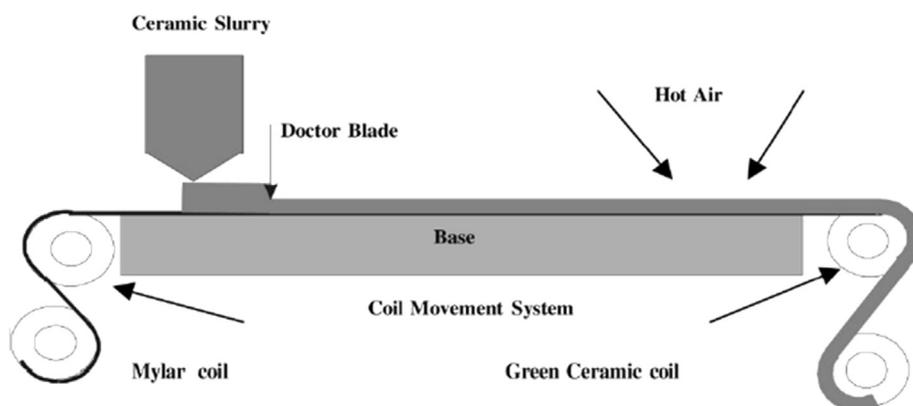


Fig. 4 – Tape-casting method of ceramic fabrication process [3].

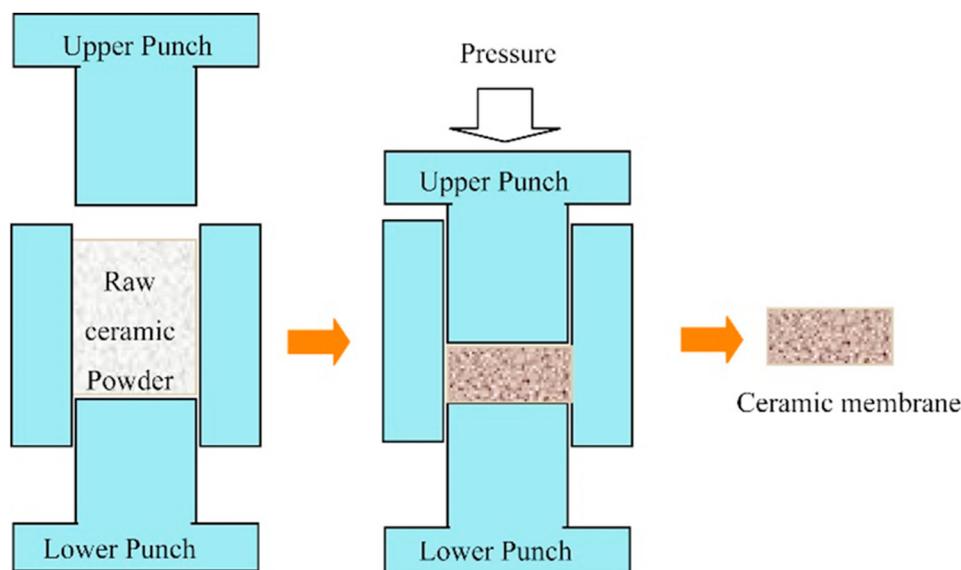


Fig. 5 – Schematic illustration of the pressing method of ceramic fabrication [4].

internal surface of the mould. Finally, a solidification step is carried out rapidly to hinder the passage of particles into the pores [73–76]. Fig. 3 shows the schematic illustration of the slip casting technique. On the other hand, the tape casting technique is employed for fabricating flat sheets ceramic membranes with large surface areas and thin pieces of 0.02–1.3 mm [77]. The method is very similar to the casting technique that is applied in the fabrication of polymeric flat sheets membranes. The casting technique emerges as a result of the growing interest in electronics industry applications. Fig. 4 shows the basic principle of the tape casting process. The process comprises of a fixed casting blade, dope suspension reservoir, moving carrier and drying motor zone [73].

The pressing technique is commonly practiced in fabrication of disc kind of ceramic membranes for application in basic research. It uses precise pressure to shape and compress the granular powders which are mixed with additives in a flexible mould [78,79]. Fig. 5 shows the process of particle consolidation to a dense layer as a result of an applied force. More than 100 MPa pressure can be applied using a particular press machine to press the granular powders into a more condensed disc shape. The disc diameter can be up to few centimeters with 0.5 mm thickness, and densification of the disc will be occurred after firing [62]. In general, the process of operation of pressing is made up of three steps: i) mould filling, ii) dough compaction and iii) piece extraction. The pressing has its drawback due to mechanical stress as the membranes are being compacted caused the pressure increase thereby results into defects and cracks formation [80].

The extrusion technique of ceramic fabrication is a well-known method used in fabricating large products weighing up to 1 ton as well as small products of a few grams [81]. As illustrated in Fig. 6, the process of extrusion is comparable to the process of spinning the fiber; nevertheless, few differences are observed between the two processes. In the extrusion process, force is used to shape a compacted stiff paste through a nozzle, and the requirement is that precursor material should possess a plastic behavior that is rigid at lower stress

and deform at yield stress. While in the spinning process, the spinneret is used to transform a dope suspension to a stable shape in a coagulation bath. The extrusion technique has limitations in terms of size variances and configuration limitations. The size variance due is to unpredictable geometry formation from different extrusion parameters and deficient in configuration will require expanding the extrusion equipment to accommodation different configurations [82].

The early stage of development of the hollow fiber phase inversion technique for ceramic membrane fabrication was reported by Luyten et al. [83] for the production of cost-effective oxygen. This method was achieved by modifying the hollow fiber technique for polymeric membrane with a

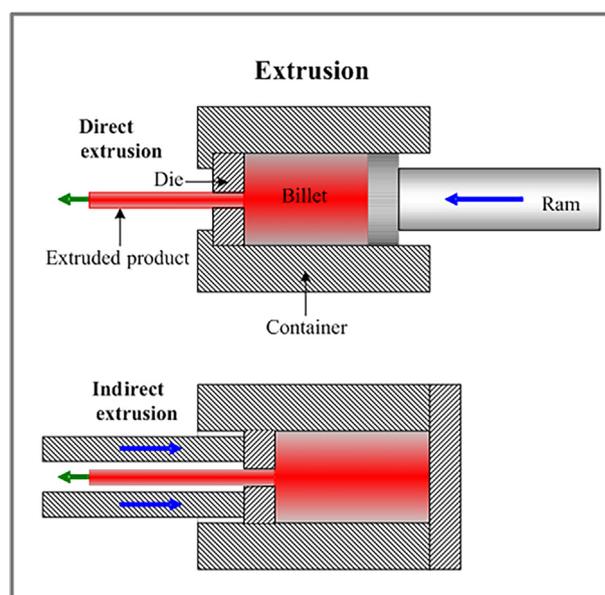


Fig. 6 – Extrusion method of ceramic fabrication [5].

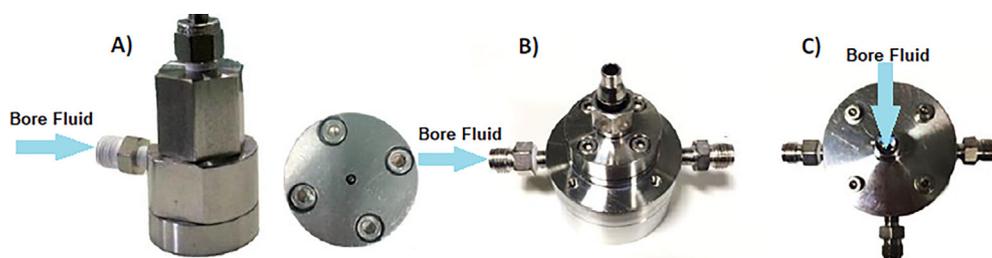


Fig. 7 – Kinds of spinneret (A) Double orifice [55] (B) Triple orifice [116] and (C) Quadruple orifice [121].

mixture of suitable ceramic powders as the main constituent, while the polymer content was reduced to a minor component. The presence of minor amount of polymer in the mixture will act as a binder and hereafter will be burned-off at the sintering process. The mixture is referred to as dope suspension and is prepared by milling ceramic powders with solvent for 24 h, after which the polymer will be added and will be mill further for 48 h to ultimately have fully homogeneity of the mixture. Afterward, the dope is extruded via a double cylinder nozzle into non-solvent bath. Currently, there are spinneret with both double [71,84,85] and triple orifice [86–90] for respective fabrication of single- and double-layer ceramic hollow fiber membranes. Moreover, also, recently, Kang Li's research group (Imperial College London) has successfully designed a quadruple orifice for the producing a triple-layer ceramic membranes [91]. Fig. 7 depicts the three different kinds of spinneret. After spinning the dope suspension into the non-solvent coagulant, the precursor ceramic hollow fiber will be cut to a certain length and drying at room temperature. Lastly, the precursor ceramic hollow fiber membrane will be subjected to the sintering process in order to burn off the added polymer (at 600 °C) and allow consolidation as well as growth between the ceramic particles (1225 °C and above). Fig. 8 shows the schematic spinning

process of hollow fiber ceramic membrane fabrication via the phase inversion. The disadvantage of hollow fibre membrane is that it is susceptible to fouling and pore plugging by particulate matter due to relatively small space between fibre and membrane diameters [92].

3. Natures superhydrophobic surfaces

In nature, many superhydrophobic surfaces are typically found in some plants, animal and insect species which both possesses mimesis, water active and self-cleaning properties for better survival in the environment [16,93,94]. The natural superhydrophobic surfaces are mainly for the purposes such as prevention of water accumulation, encapsulation of contaminants on their surfaces for droplet rolling, lesser adhesion to irrelevant substances and to prevent microbial growth. The surfaces of substrates are superhydrophobic because of the geometrical arrangement of the micro-nano structures which makes the water droplets rolled off smoothly on the surface and hence give it self-cleaning effect [95]. The self-cleaning features found in some plant species is used mainly to remove liquid and solid contaminants which could interfere with the process of photosynthesis. The antiwetting features

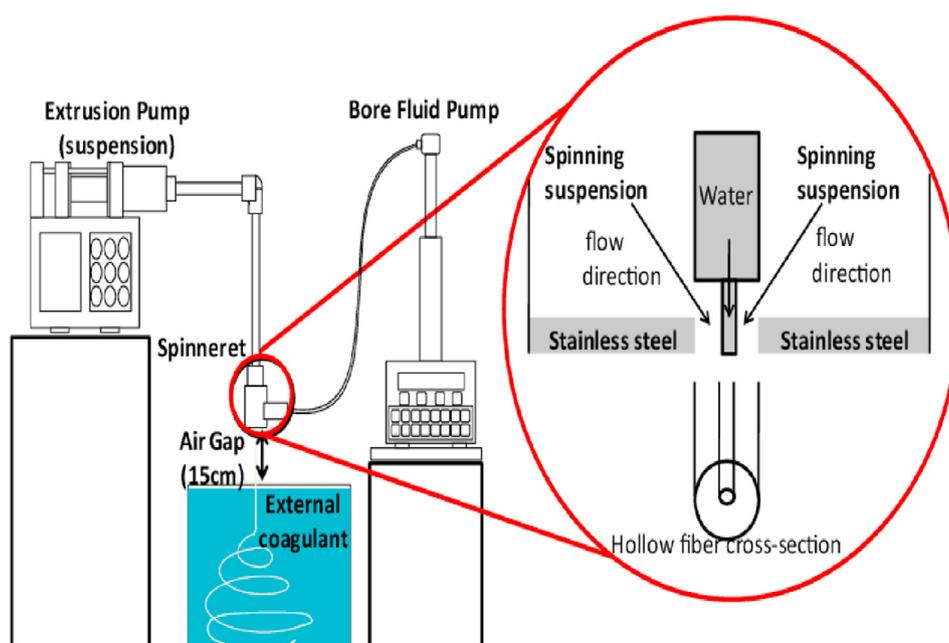


Fig. 8 – Schematic illustration of hollow fiber ceramic membranes fabrication process [6].

found on the surface of mosquitos' eyes aids for anti-fogging. Also, the superhydrophobic layer found on the cuticle of a planthopper insects wings serves as anti-bacterial protection [96]. In all of these scenarios, the rolled off in fluid flow and the self-cleaning properties are contributed by the low contact angle hysteresis [97].

Studies have found that the superhydrophobic properties in nature is not actually from the respective chemical diversities but rather from the structural arrangements of the building blocks [93]. The designs of the superhydrophobic surfaces are made of four general groups which are i) shapes with varied micrometres usually in one dimension, (ii) dome shape and simple pillars, (iii) hierarchical structural organization (iv) setae or hair with length greater than 5 μm and lesser diameter [98]. It important to note that, the superhydrophobic surface is formed as a result mainly hierarchical micro-nanostructures and low surface energy [99]. For instance, the lotus leaf which is known as the most typical plant with thousands of micro-papillae structures on its surface which when annealed to reduce the abundant micro-structure properties. The water contact angle of the annealed lotus leaf was found to be reduced which inferred that the presence of the abundant rough microscale surface and hair-like nanoscale structures result in having higher water contact angle [100].

Guo and Liu [101], investigated eight different leaves of superhydrophobic plants by dropping water droplet on individuals' leaf. The superhydrophobicity of the leaves were examine using water contact angle test and scanning electron microscopy analysis for morphological view. Amongst the leaves, India canna leaf possesses the highest water contact angle of 165° while rose petal shows the least contact of 152.4° among the investigated leaves. In other words, all the leaves attained the superhydrophobic properties thereby achieving water contact angle greater than 150° . It was also concluded that the, the leaves possesses hierarchical micro-nanostructure and unitary nanoscale or subscale which contributes to the formation of the superhydrophobic layers.

Aside from the plants, many phenomena of special surface antiwetting features in animal kingdom are being reported in the literatures. A group of scientists report their work on the wetting and microstructure characteristics of the wings of 97 insects [102]. The researchers claimed that most insect wings have superhydrophobic as well as self-cleaning features which is responsible for their stable flight in humid environment to prevent accumulation of water droplets and dust. Another group of scientists published their work on the morphological structure of different species of cicada wings [103]. The water contact angle results showed a remarkable variance in the anti-wettability features among their respective cultivars which could be due to chemical composition as well as the surface morphology of the nanostructures. Similarly, the presence of the waxy layered structures coated on the surface of the insect wings could contribute to the anti-wetting properties of the wings as reported by Gao et al. [104]. In addition to insect wings, the feet of some insects are reported to have superhydrophobic features. Recently, studies discovered that the wall gecko's feet have superhydrophobic features with extremely adhesive force of about 60 mN [105]. These features were examined by dropping water droplets on

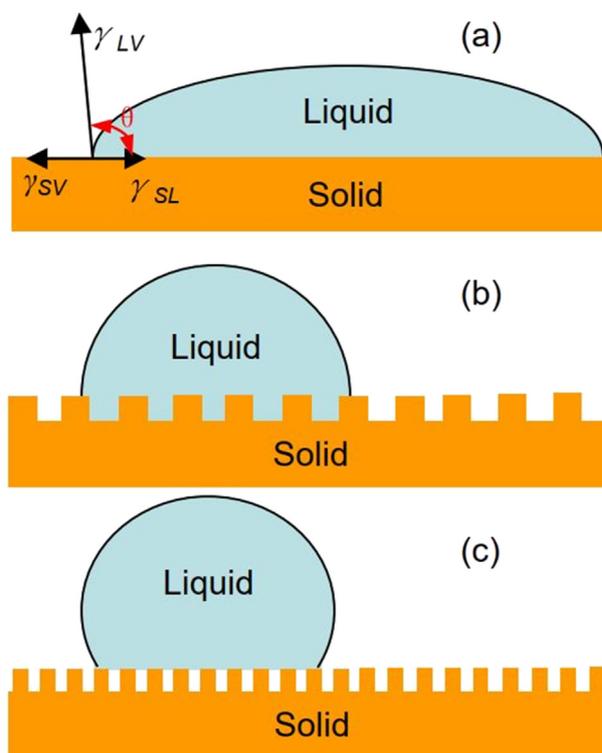


Fig. 9 – Schematic illustration of liquid droplets using Young's (a), Wenzel (b) and Baxter-Cassie (c) models [7].

the feet of the gecko where the droplets were found to stand still adhered to the feet even after turned upside down. The extreme superhydrophobic properties were believed to be due to the presence of number of an orderly micro bristle structure present on the gecko's feet.

4. Characteristics of superhydrophobic surfaces

Superhydrophobic-superoleophilic materials are preferred in the absorption of the low surface tension oil molecules. However, ceramic membranes are rich in hydrophilic groups thus tend to absorb water molecules [106]. To enhance oil molecules absorption of ceramic membranes, hydrophobic-oleophilic modification is required. Surface modification of ceramic membrane is the approach that can be used to improve the wettability and antiwetting property of a membrane through the decrease of surface free energy. There are several reports on various chemicals used in lowering the surface energy of a substrate which include; organophosphonic acids, steric acids, fatty acids, alkanethiols and organosilanes [107–113]. Organosilanes are the most widely and frequently used chemicals in both research and technology for alignment of proper surface topology and lowering of substrate surface energy through the hydrolytic condensation of tetraethoxysilane (TEOS) and organosilanes. It is preferred due to its simplicity, creation of superhydrophobic-superoleophilic substrate, cost-effectiveness and less toxicity [114].

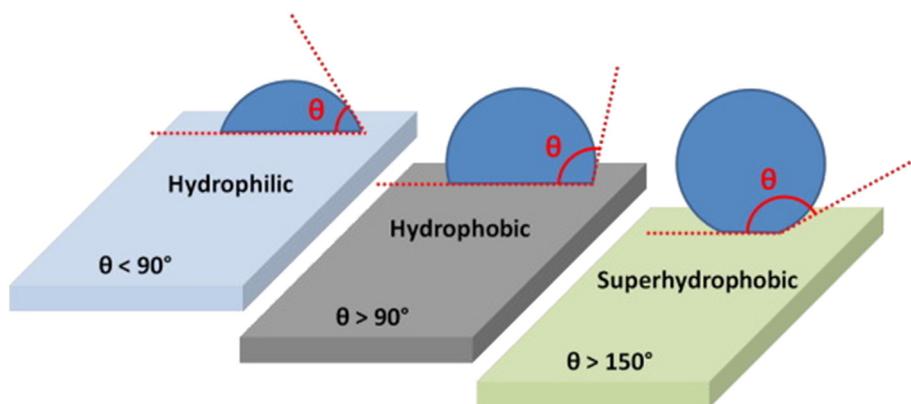


Fig. 10 – Water contact angles of hydrophilic, hydrophobic and superhydrophobic substrates [8].

A porous ceramic membrane surface that strongly repels the passage of water droplets is called a superhydrophobic surface. The degree of superhydrophobicity of a surface is commonly determined by measuring the water contact angle and water contact angle hysteresis [115]. Contact angle (CA) can be used to measure the wettability of the surface while contact angle hysteresis is used to measure the level of stickiness of water droplet on the ceramic membrane surface. When a water drops on ceramic membrane surface, it is expected for water to either spread completely on the ceramic membrane surface or it rest on the surface without having significant contact with the surface. This phenomenon is referred to as completely hydrophilic or hydrophobic surfaces. It is important to note that; water droplet can easily roll off if the ceramic membrane surface possess a high contact angle and less contact angle hysteresis. For a substrate surface to possess a superhydrophobic property, the contact angle of the substrate must be $> 150^\circ$ and the contact angle hysteresis must be $< 10^\circ$ contrary to this will hence be hydrophobic or hydrophilic. Physically, if a liquid drop on the surface of solid ceramic membrane, there exist three interfaces; solid–liquid, vapor–solid, and vapor–liquid which will subsequently lead to three surface tensions as; 1) γ_{SL} , 2) γ_{LV} , and 3) γ_{SV} (Fig. 9a). In 1805, Young [116] formulated an equation with which shape of a fluid droplet on a smooth solid substrate surface can be evaluated using Eq. (1) below.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_Y \tag{1}$$

where γ_{SL} , γ_{LV} and γ_{SV} are the respective interfacial surface tensions between solid–liquid, liquid–vapor, solid–vapor meanwhile θ_Y is the contact angle between the liquid and solid. Surface tension is a significant parameter which aid the forming an interface or boundary between two different phases (e.g. solid and liquid phase). For a liquid drop to spread completely on a solid surface, values of the solid surface tension is required to be higher hence will result in having contact angle $\leq 90^\circ$ on the other hand, low solid surface tension will tend to make the liquid droplet rest on the solid surface with a spherical shape and contact angle of $> 90^\circ$ (Fig. 10). However, for a completely hydrophobic liquid droplet, the contact angle is expected to be up to 180° and 0° for a completely hydrophilic liquid droplet [117]. Contact angle of solid surface can be evaluated using Eq. (2).

$$\cos \theta_Y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{2}$$

Eqs (1) and (2) are only applicable for solid surface with a smooth surface such as polymeric membrane with exception of solid with rough surfaces such as ceramic membrane [118]. For this, Wenzel formulated a relationship between contact angle and roughness. He modified the Young’s equation thereby introducing a roughness factor, r_s , which is the ratio of rough and smooth surfaces as shown in Eq. (3) below.

$$\cos \theta_W = r_s \cos \theta_Y \tag{3}$$

where θ_W is the apparent contact angle. The apparent contact angle is used to determine contact angle of rough surfaces. Wenzel claims that, increasing the roughness of a solid surface area will slightly increase the surface tensions of solid–liquid and solid–vapor interface while the interfacial surface tension of liquid–vapor remain constant [119]. Consequently, higher contacted angle is achieved to balance the increased in the surface tension due to the increase in surface roughness making the roughen surface to be superhydrophobic.

Wenzel model was able to only discuss rough solid surface without addressing porous solid surfaces, for this, Cassie and Baxter extended the model in order to accommodate porous surfaces [120]. In the case of Wenzel model, the higher the surface roughness then the more the liquid droplets completely filled in the solid surface (Fig. 9b). This is not same in Cassie and Baxter model, instead, a mass fraction of a liquid droplets will be in contact with the higher peaks of the rough solid surface resulting in liquid–solid interface while less fraction make contact with vapor therein the valleys resulting to liquid–vapor interface as shown in Fig. 9c. Eq. (4) below is referred to as Cassie–Baxter equation.

$$\cos \theta' = f_1 \cos \theta_Y - f_2 \tag{4}$$

where f_1 and f_2 are respectively represents the air and surface fraction, and θ' is the Cassie and Baxter improved apparent contact angle for porous surfaces. Existence of pores on a solid surface will at all times increase the contact angle. Hence, an apparent contact angle of 90° can be transformed to 150° by introducing pores on the same solid substrate surface [121].

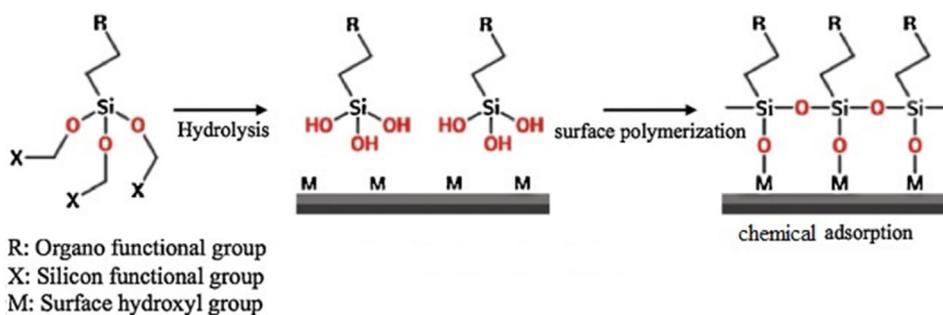


Fig. 11 – Bonding mechanism of silane coupling agent onto the ceramic membrane surface [9].

The morphology or surface texture is another vital parameter apart from the contact angle and the contact angle hysteresis that were used in transforming hydrophobic surfaces to superhydrophobic surfaces. The surface morphology of a ceramic membrane can be made up of micro and/or nanoscale textures that contain mushroom-like or overhanging structures which hence contribute to the surface roughness [122]. The presence of micro-nanoscale structures results in trapping air in between the voids spaces of the mushroom-like structures. Due to this, the Cassie and Baxter model can be realized hence superhydrophobicity is achieved. This is to say, the surface morphology or texture plays an important role in producing superhydrophobic substrate [123].

It is very possible to transform a hydrophilic substrate such as ceramic membrane fiber into superhydrophobic substrate. According to Herminghaus [124], substrate hydrophilic material possessing contact angle $<90^\circ$ can be transformed to a super water repellent material. Hence, with an appropriate morphology or texture, hydrophilic surfaces can be converted to superhydrophobic surfaces. For example, Wu and co-workers [125], prepared micro and nanoscale roughened zinc oxide surface by alkaline hydrothermal treatment. The surface initially exhibited a superhydrophilic with water contact angle of almost 0° however, after spin-coated with Teflon, double roughness was created hence the surface was converted to a superhydrophobic substrate surface with water CA of 168° . Also, Feng et al. [126] turned a hydrophilic polyvinyl alcohol film with contact angle of 72.1° to superhydrophobic polyvinyl alcohol film with contact angle of 171.2° this was achieved by addition of polyvinyl alcohol nanofibers. Additionally, by addition of silicon nanofibers, Cao and co-workers [127] transformed hydrophilic hydrogen-terminated silicon surface with 74° contact angle to a superhydrophobic substrate surface with 160° water CA.

Asides from use of contact angle, the liquid entry pressure (LEP) is another usually used parameter in characterizing hydrophobicity of ceramic membranes [128,129]. LEP is referred to as the limit of pressure requires for a fluid solution not to pass through pores of the membrane. In other way, fluid solution should not wet the hydrophobic membrane pores below a given pressure. Test using LEP is performed by pressurizing a liquid solution in order to penetrate into a membrane. However, the liquid penetration is governed by factors which includes; pore size, liquid concentration, organic solutes presence in the liquid solution, temperature and liquid

surface tension [130–132]. It is good to know that, membrane with bigger pore sizes will tend to have low LEPs as LEP is inverse of the pore size of the membranes. For membrane possessing larger pore size will get wet, if lower capillary pressure is required. Grading of hydrophobic ceramic membrane using LEP is primarily used for membrane distillation processes [133,134].

5. Ceramic membrane surface modification techniques

In recent times, there are considerable interests that pilot on the modification of ceramic membranes for improved separation performance, process development, and antifouling property enhancement. Membrane fouling happens to be the major drawback of membrane separation processes; as such, ceramic membrane surface modification can use to some extent to reduce membrane fouling, thereby hindering the interactions amid the membrane surface and unwanted feed molecules. Secondly, it is to increase membrane selectivity for specific separation purposes [29]. Superhydrophobic ceramic membrane can be achieved by an appropriate choice of low surface energy, roughness, and surface texture. This is produced by binding or attaching hydrophobic materials such as silanes used for ceramic materials and glass, acids for magnesium, halogenated or hydrocarbon thiol for silver and gold, and phosphates for stainless steel. Furthermore, inclusion of micro and/or nano-fibers will create an excellent rough surface to achieve a superb water-repellent feature. This will conversely help in creating surface with extreme roughness and low surface energy, more also, will aid in improving the affinity as well as the responsiveness of the membrane for the desired application. There are four ways commonly used techniques of surface modification of ceramic membrane which are immersion, chemical vapor deposition (CVD), sol-gel, and lipid solution direct grafting method.

5.1. Immersion technique

The immersion technique is a time-saving and straight forward procedure that requires only cheap chemicals to produce hydrophobic ceramic membranes. The method is facile as it requires no special equipment, but rather, a pristine membrane is dipped directly into a reactive hydrophobic solution. Ceramic membrane immersion is done by a

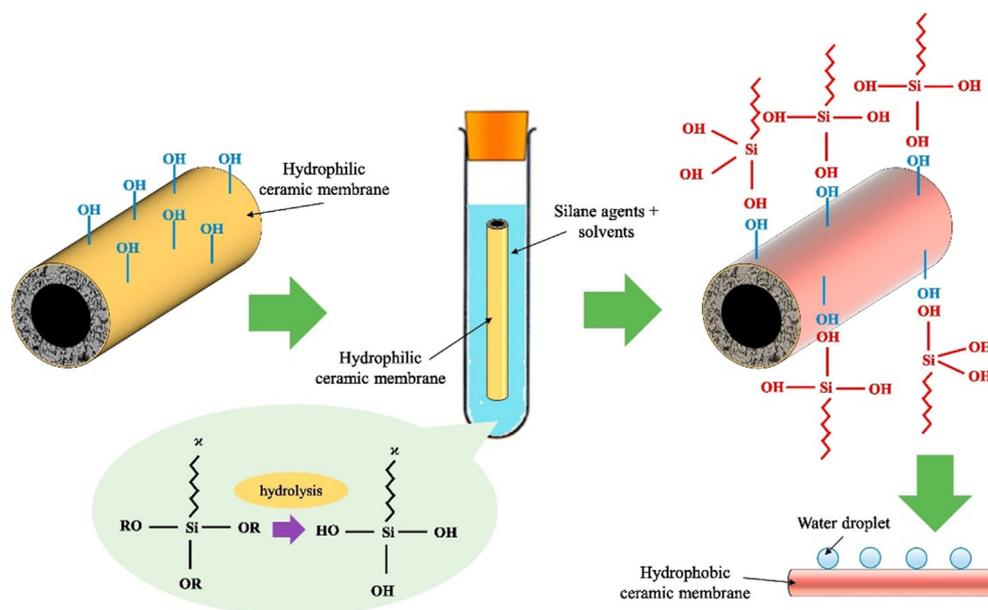


Fig. 12 – Schematic illustration of immersion technique of surface modification [10].

condensation reaction between the functional group of silanes and OH groups that resides on the surface of the ceramic membrane. Prior to the immersion of the substrate, hydrolysis of organosilane in solvents like water, alcohol or hexane in order to produce reactive organosilane solution with active silanol. Then followed by immersing the pristine membrane into solution of active silanol, subsequently the reactive organosilane molecules are chemically absorbed on the membrane surface. Fig. 11 shows the reaction pathway on how active silanol species are formed via hydrolysis of the organosilane insolvent, by converting the reactive substituent such as halogen and alkoxy groups present in the organosilane molecules to OH groups [135–137]. After the immersing membrane into the organosilane solution, the membrane surface will tend to chemisorb the excess Si–OH compounds, which will further link up with other nearby silane molecules forming Si–O–Si bond. As a result, the Si–OH chemically absorbed molecules will eventually form a uniform and thin film [138,139]. The intermolecular interactions and chemical bonding will lead to establishment of an active immobilized molecule on the membrane surface which will enhance the mechanical and chemical stability of the hydrophobic membrane. The impact of this technique for hydrophobization of the ceramic membrane is greatly influenced by organosilane concentration; the number of hydroxyl groups presents on the surface of the ceramic membrane, coating duration, number of grafting cycle as well as surface roughness of the membrane [131]. However, organosilane concentration is the most crucial factor in preparing hydrophobic ceramic membrane as the quantity of active organosilane species reacting with the abundant hydroxyl groups presence on substrate surface lies on the concentration of the reactive organosilanes. Therefore, the reaction solely depends on the amount of hydroxyl groups presence on the ceramic membrane surface. But highly concentrated organosilane solution will trigger the production cost due to high purchasing cost of the organosilane.

Development of superhydrophobic ceramic membrane can be achieved by repeating the organosilane immersion cycles to create super-complex molecules on the substrate surface. Conversely, multiple immersions to certain extent will encourage membrane pore shrinkage and this will result to mass transfer resistance. The number of grafting cycles on the substrate surface should be precise so as to yield a superhydrophobic membrane with less mass transfer resistance.

Kong et al. [140] fabricated a superhydrophobic surfaces on copper substrates via novel solution-immersion technique. In the study, they prepared a slice like $\text{Cu}_2(\text{OH})_3\text{NO}_3$ crystal on a copper foil surface by of immersion in an aqueous solution of cupric nitrate and sodium hydroxide. The superhydrophobic surface was created by altering the slice-like $\text{Cu}_2(\text{OH})_3\text{NO}_3$ crystal with solution of 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FAS-17). Kujawski et al. [141] studied the effect of immersion conditions for modification of ceramic membrane. The ceramic membrane precursor was initially rinsed with acetone, ethanol, and water, then subsequently; dried ceramic membranes were immersed in FAS of different concentrations at variable grafting time in order to study the effects of coating conditions. LEP measurement was used to determine the effectiveness of the grafting parameters. The result shows a higher LEP at increasing the value of grafting parameters. Also, the result shows a strong correlation between LEP and water flux. Liu et al. [142] produced a firm superhydrophobic films on zinc substrates material by a simple immersing the zinc substrate into a hydrolyzed solution of 1H,1H,2H,2H-perfluorooctyltriethoxysilane [$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$, PFTS] consecutively for 5 days at ambient temperature and was then hardened in hot air of 130 °C for 1 h. The coated superhydrophobic film layers on the zinc interface provides strong resistance to deterioration when it is immersed in an aqueous solution of sodium chloride for 30 days. In another similar study, Lu et al. [142] fabricated FAS-grafted

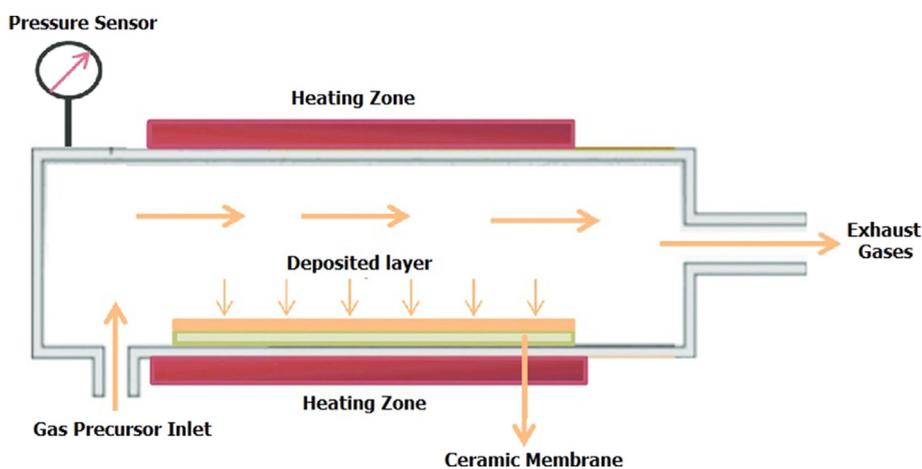


Fig. 13 – Schematic illustration of CVD technique of surface modification [11].

superhydrophobic alumina membrane, which was test-run prior to immersion into FAS solution, and the solution of sodium hydroxide solution eroded the pristine alumina membrane. By controlling this, the concentration of FAS solution, grafting cycle, and coating time leads to formation of superhydrophobic alumina membrane with a great water contact angle of 164.53° and hence there is resistance to erosion when immerse in NaOH solution. Khemakhem et al. [143] fabricated superhydrophobic zirconia membrane there by grafting C88 molecules onto the surface of zirconia membrane. Water contact angle (WCA) was observed to be increased from less than $20\text{--}160^\circ\text{C}$. Fig. 12 depicts the schematic pathway of immersion technique of surface modification.

5.2. Chemical vapor deposition technique

The chemical vapor deposition (CVD) is an extensively and frequently technique used in developing nonvolatile thin solid-film coatings onto a substrate surface [144–148]. The technique involves the use of chemical reactions of gaseous species within the vicinity of the heated substrate surface; the modifying agent vaporize by heat. Afterward, the vaporized modifying agent reacts with the OH groups on the ceramic membrane surface, this is same as in the immersion technique. Fig. 13 depicts a schematic illustration of the CVD process of surface modification. The method is effective and preferred process in producing micro or nanoparticles, nanorods into an orderly macroscopic structure; the method also has a higher tendency of using different as well as a wide range of chemical reagents. However, there are some factors that need to be into consideration prior to performing CVD grafting which includes; concentration and organosilane to be used, boiling points of the solvent and organosilane to be used as heat is involved in the process, closed vessel volume to be used and finally coating time [131].

During the CVD process, the organosilane solution and the ceramic-based membranes substrate will be placed into a sealed container. Then will be subjected to heating at boiling point of the reactive organosilanes for quite some hours. The

vapor evolved from the organosilane will react with hydroxyl group on ceramic membrane surface. To achieve maximum reaction between the ceramic membrane and the organosilane vapor, there is need to select a suitable size of the closed vessel for a better alignment of the ceramic membrane samples. Also, optimization of the grafting time is necessary to be considered as organosilane molecules have distinct reaction time and chemical properties.

Hozumiet al. [149] investigated the tuning of the dynamic wettability of oxidized alumina and titanium surfaces through a chemical vapor reaction of 1,3,5,7-tetramethylcyclotetrasiloxane ($\text{C}_4\text{H}_{16}\text{O}_4\text{Si}_4$). This was achieved by regulating the temperatures of the CVD as such the oxidized hydrophilic aluminium and titanium surfaces transformed into low-hysteresis superhydrophobic surfaces. Li et al. [150] developed a long tubular carbon-coated ceramic membrane via pyrolysis of methane using CVD technique. From the results, it shows that the grafted ceramic membrane exhibited a kind of unvarying carbon coated membrane with an anticipated pore size; thus, this indicates the capability of CVD technique not only to hydrophobized material but yet to control the membrane pore size that could be used for various application. Rezaei et al. [151] successfully grafted a superhydrophobic material with a high water contact angle (WCA) greater than 160° and a low 5° sliding angle (SA) by simultaneously using CVD technique and silica nanoparticle modification method using triethoxysilane, vinyltrimethoxysilane (VTMS) and ammonia. Sugimura et al. [152] prepared self-assembled monolayers organosilane on a ceramic membrane surface by using three different types of organosilane viz n-(6-aminohexyl) aminopropyltrimethoxysilane (AHAPS), fluoroalkylsilane (FAS), and n-octadecyltrimethoxysilane (ODS). After the solutions of the three organosilanes and the ceramic membrane were placed in an oven vessel of the temperature of $100\text{--}150^\circ\text{C}$. The resultant maximum contact angles achieved as a result of coating with FAS, ODS, and AHAPS are 112 , 105 and 62° , respectively. FAS happens to generate the highest water contact angle because due to high hydrophobic molecules present in the FAS chain which

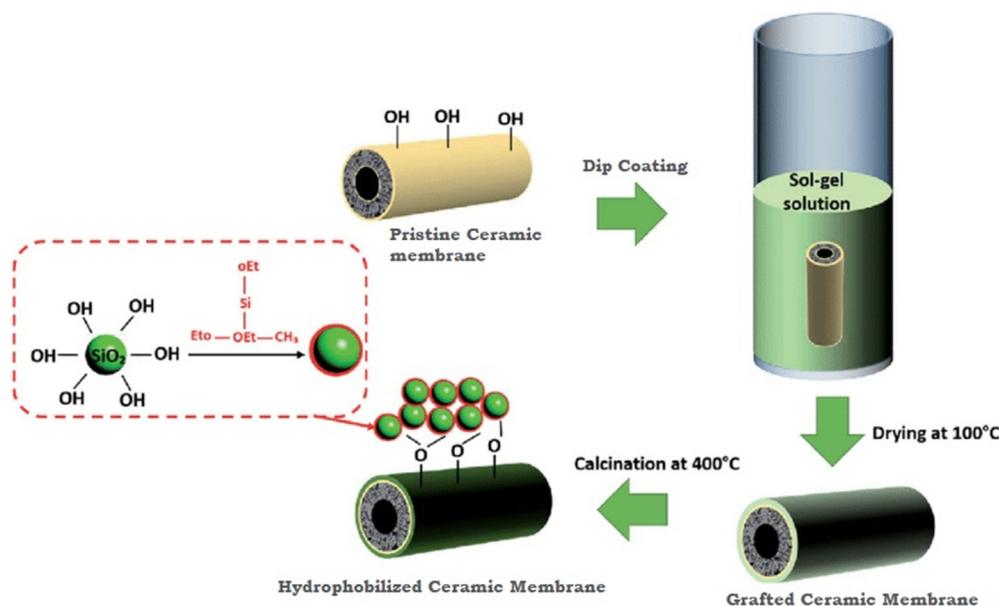


Fig. 14 – Sol–Gel Grafting process of the ceramic membrane [12].

can affect the hydrophobic coating behavior due to the lengthy chain of fluorocarbon [153]. Superhydrophobic carbon fabric with micro/nano-scaled two-tier roughness was fabricated by decorative carbon nanotubes (CNTs) onto micro-sized carbon fiber using catalytic chemical vapor deposition with subsequent fluorination treatment of the surface. Through the introduction of the CNTs, the water contact angle keeps increasing (148.2–169.7°) hence, this study shows a superhydrophobicity property of a carbon surface with resemblance of the lotus leaves found in flora [154]. The CVD technique and methyltrichlorosilane (MTS) solution was used to coat PVDF membrane by Zheng and CO-workers [155]. Pretreatment using oxygen plasma was made on the PVDF membrane. Before the CVD process, this will help in creating an active group that will react with the solution of MTS to produce a polymethyl siloxane layers. The water contact angle and the sliding angle of the modified PVDF membrane, are 155° and 4° respectively hence exhibiting superhydrophobic features. Li and Co-workers developed a novel A-Si₃N₄ planar nanowire superhydrophobic membrane via in-situ nitridation. Contact angle of 160° was achieved with higher flux of 8.09 lm⁻²h⁻¹ at 90° and the flux was maintained for 500 h [16].

Used of CVD in producing superhydrophobic ceramic membrane is quite an easy technique, however, there some weaknesses with technique. CVD is restricted to specific organosilane agents with low boiling point; the process requires loss of energy and time consumption when selecting an optimum vessel size to be used. Also, it requires special safety precautions as organosilanes are toxic chemicals.

5.3. Sol–gel technique

The sol–gel method is used to create hydrophobic coating with great roughness on the ceramic membrane, thereby mixing organosilane with sol–gel [146,156,157]. The process involves network formation that occurs by simultaneous

hydrolysis-polycondensation of the precursor oxides to form a glassy gel material. The sol can be directly applied to the ceramic membrane or can be combined with silica nanoparticles to serve as the fillers. The coated ceramic membrane surface roughness can be altered by manipulating certain conditions of the system and reaction rate of the mixture, according to Xue et al. [5]. It is good to note that early introduction of organosilane into the sol solution could result in the formation of bulky polymer which will slow down the formation of microporous hydrophobic ceramic membrane. Compared to CVD and immersion techniques, the sol–gel method requires a longer time to prepare the sol solution, and afterward, the coated membrane needs to undergo calcination process to remove the sol–gel templates. The process of dip-coating of the ceramic membrane substrate via sol–gel technique is illustrated in Fig. 14 below.

Yang et al. [158] successfully grafted ceramic membrane via simple dip-coating the membrane into solution of sol–gel prepared from a bis-silyl precursor. The grafted ceramic membrane was able to transport ammonia on the water by separation factor of 12 while maintaining a stable flux for 7 h. The sol–gel method was used to induced superhydrophobic/superhydrophilic properties on tubular ceramic membrane surface for oil recovery; this study was carried out by Suet al. [159]. The sol–gel solution was made by mixing tetraethoxysilane (TEOS), ammonia, distilled water, and ethanol at a concentration of 0.41, 1.05, 3.56 and 13.90 mol, respectively for 90 min at 30 °C. The prepared methylated silica sol–gel was allowed to age for one week for gelation creation. After that, the tubular ceramic membrane was then dip coated into the gelled sol solution for about 2 h at ambient temperature and then subsequently was oven dry at 110 °C for 30 min. De Vos and coworkers [160] fabricated hydrophobic silica-based membrane via dip coating the membrane into a sol–gel solution composed of methyltriethoxysilane (MTES). The grafted membrane hydrophobicity was enhanced for 10 consecutive times after removing the sol template by the aid of calcination

Table 2 – Summary of hydrophobic surface modification of ceramic membrane fabrications processes [172–174].

Features	Immersion	CVD	Sol–Gel	Lipid-Solution
Cost-effectiveness	The method is cost-effective as almost 98.1 wt. % of the prepared silane agent solutions are solvent	Less amount of organosilanes solution and solvents are required as reaction undergo vaporization	For more cost cut, other chemicals can be employed to produce silane solution	This method is cheaper as compared to others since ordinary vegetable oils can be used.
Roughness formation	Nano-particle coating	Nano-structure growth by polymerization	Nano-particle growth by silica	Nano-particle by vegetable oil
Energy	Requires drying at 60–100 °C thus less energy is consumed	Heat is applied to vaporize the silane agent	Requires calcination at temperature 400–500 °C after dip-coated	No calcination is required
Time	The hydrophobicity of the membrane is enhanced if the grafting time is long	The hydrophobization process very fast as it involves vaporization of the silane agent hence the process is hazardous	The process consumes lots of time because of the number of repeating steps involves excellent grafting homogeneity	This technique is quite fast and straightforward as it requires a mixture of oil and solvent to form the lipid solution
Morphology	The morphological structure is slightly altered	Slight morphological adjustment due to change in shape and size	The structure looks more of lotus leaf as a result of nano-silica presence on the substrate surface	No significant changes in the structural view
Properties	The stability is quite high depending number of usages. It is reported to last for a few weeks.	It is reported that the firmness or stability may be same to that of immersion technique as no stability test done so far	Stability is low at high temperature	High thermal stability due to rich molecular design flexibility

at 400 °C for 4 h. The studies also show that the wettability behavior of the grafted membrane is affected significantly with respect to the molecular orientation of the sol–gel.

Purcar et al. [161] successfully produced fluorinated silica nanoparticle through a sol–gel process, which was coated on a glass slide to form hydrophobic films. The coworkers lament that, with proper experimental conditions of the system, the experiment can be reproduced for a large-scale industrial application and hence, the derived fluorinated silica nanoparticles will serve as an engineering material. Ahmad et al. [162] fabricated superhydrophobic alumina membranes by dip-coating the membranes into a sol–gel solution and then followed by grafting with triethoxysilane. The coated membranes were further treated with the water treatment temperature of 100 °C and optimal steam impingement duration of 1 min in order to create more porosity and more roughen surface. The water contact angle of the fabricated superhydrophobic alumina membranes is 158.4 °C, while the resistivity of the membrane is $139.5 \pm 24.9 \text{ Gm}^{-1}$. Su et al. [163] also used the sol–gel technique to coat a ceramic membrane and then followed by surface grafting with polyurethane-polydimethylsiloxane. The modified ceramic membranes exhibit dual properties of superoleophilicity and superhydrophobicity with a water contact angle of 161.2 °C and an

oil contact angle of 0 °C. Guray et al. [164] fabricated transparent self-cleaning superhydrophobic coatings by a simple one-step sol–gel approach via a chemical reaction of long-chain fluoroalkylsilane. The surface morphology of the coatings exhibited a high surface roughness with wrinkled as well as hill-like morphology. The water contact angle of the surface was measured to be 169° with a sliding angle of 5° which gave the water droplet a spherical shape.

Sol–gel coating method can be able to produce a stable superhydrophobic surface; conversely, the pore size of the dip-coated membranes will tend to reduce depending on the number of coating cycles and also calcinations at a higher temperature will distort the integrity of the membrane and also reduced the membrane hydrophobicity features.

5.4. Lipid solution direct grafting

Oils from vegetable are low-cost, most abundant in colossal quantity and are a form of organic oils which is most important. Studies have shown that oils from vegetables can also be used for coatings applications due to its unique properties that comprise rich in molecule interfere flexibility, less absorption of moisture, and exceptional thermal stability [165–167]. Lipids are made up of fatty acids with significant

long chains of both mono as well as poly-unsaturated acids. The structural interface of fatty acids consists of carboxylic groups (-COOH), which can react directly with the hydroxyl group (OH) found on pristine ceramic membrane surface to the produced hydrophobic ceramic membrane surface. The lipid solutions preparation requires a mixture of vegetable oils with a specific ratio of solvent to produce the desired concentration of lipid solution. The concentration of the prepared lipid solution, as well as the type of oil and solvent, used significantly affect the properties of the grafted ceramic membrane.

Romero et al. [168] used corn oil with less than 14% w/w was mixed in dichloromethane, and then the tubular ceramic membrane was dip-coated in it to produce hydrophobic tubular ceramic membrane. As the concentration of the corn-oil was increased to 25% w/w, the ceramic membrane became plugged, thus impermeable conversely; when with corn oil was mixed with hexane solvent, the membrane performance became abysmal. Although this technique is facile, it requires no hazardous chemicals and cost-effective, yet it is commonly practiced as lipid solution preparation is only applicable to certain oils, and also, if the lipid solutions are used under a corrosive medium, the oils may not be able to degradation [169,170]. Table 2 summarized processes of hydrophobic surface medication of ceramic membrane, out of which immersion coating technique is the most promising technique due to its prevailing advantages with respect to less time require, its stability, the cost-effectiveness, and energy consumptions [168].

Other methods of superhydrophobic surfaces include chemical etching, laser etching, plasma treatment, electrochemical reaction and deposition, electron spinning, self-assembly growth etc.

Chemical etching method requires lower equipment and experimental space to fabricate superhydrophobic surface on the substrate. Qi et al. [171] fabricated hydrophobic surface by a chemical etching method, the hierarchically rough Zn surfaces was achieved with the deposition of metal ions and modified with FAS (see Fig. 15). The results show

superhydrophobic surfaces with contact angles of 161° was obtained within 5 s with copper ion-assisted chemical etching process. Guo et al. [172] reported a cross-linked of silicone elastomers with other perfluoro-polymers on aluminium alloys lotus. The hierarchical surface roughness was achieved within 2–4 h of chemical etching process while Wu et al. [173] described chemical etching time of 4 h, 15 h and 12 h after deposition in an acidic solution of aluminium metal to achieve superhydrophobic surface.

The laser etching irradiation has both capabilities to promote high surface topologies and superhydrophobic surfaces. The attribute is owing to the differences in the laser etching rates. Wohl et al. [174] reported generation of superhydrophobic surfaces using laser ablative etching of copoly (imide siloxane). The results reveal several square pillar arrays and water contact angle of 175° , indicated in Fig. 16. The low surface energy of copoly (imide siloxane) had contributed to the reduction in the inclination for lunar dust adhesion.

Electrospinning and plasma treatment are another effective approach to superhydrophobic surface coating. The electrospinning method enhances the conversion of micro-to nano-scale surface structure of fibres from the polymeric materials [175,176]. The structures of hydrophilic material created from the electron spun for superhydrophobic surface reveal roughness on nanoscale [177]. The characterization for water contact angle indicates an increase from 110° to 158° due to the trapped air in the rough surface of the substrate (as indicated Fig. 17). Studies from the superhydrophobicity of cellulose triacetate (CTA) were promoted using electrospinning and plasma treatment on fibrous mats. The CTA with only electrospinning showed good surface roughness and WCA of 142° , whereas CTA treatment with plasma treatment reached high water contact angle of 153° after plasma treatment for 60 s [177]. The AFM revealed that non-treatment CTA displayed a resemblance of a lotus leaf while the treatment of CTA at high plasma treatment, there is protrusion of the treated surfaces and subsequent collapse due to excessive surface treatment.

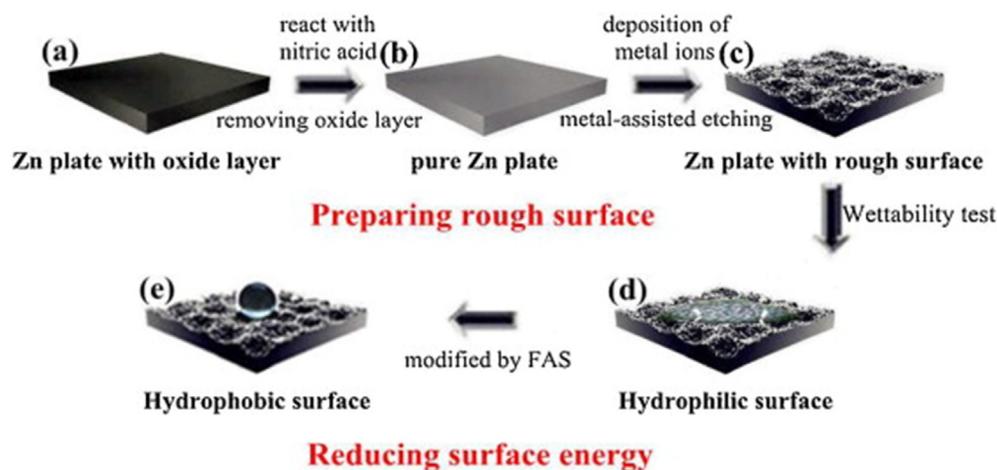


Fig. 15 – Schematic illustration of Zinc superhydrophobic surface on metal substrate using chemical etching approach [13].

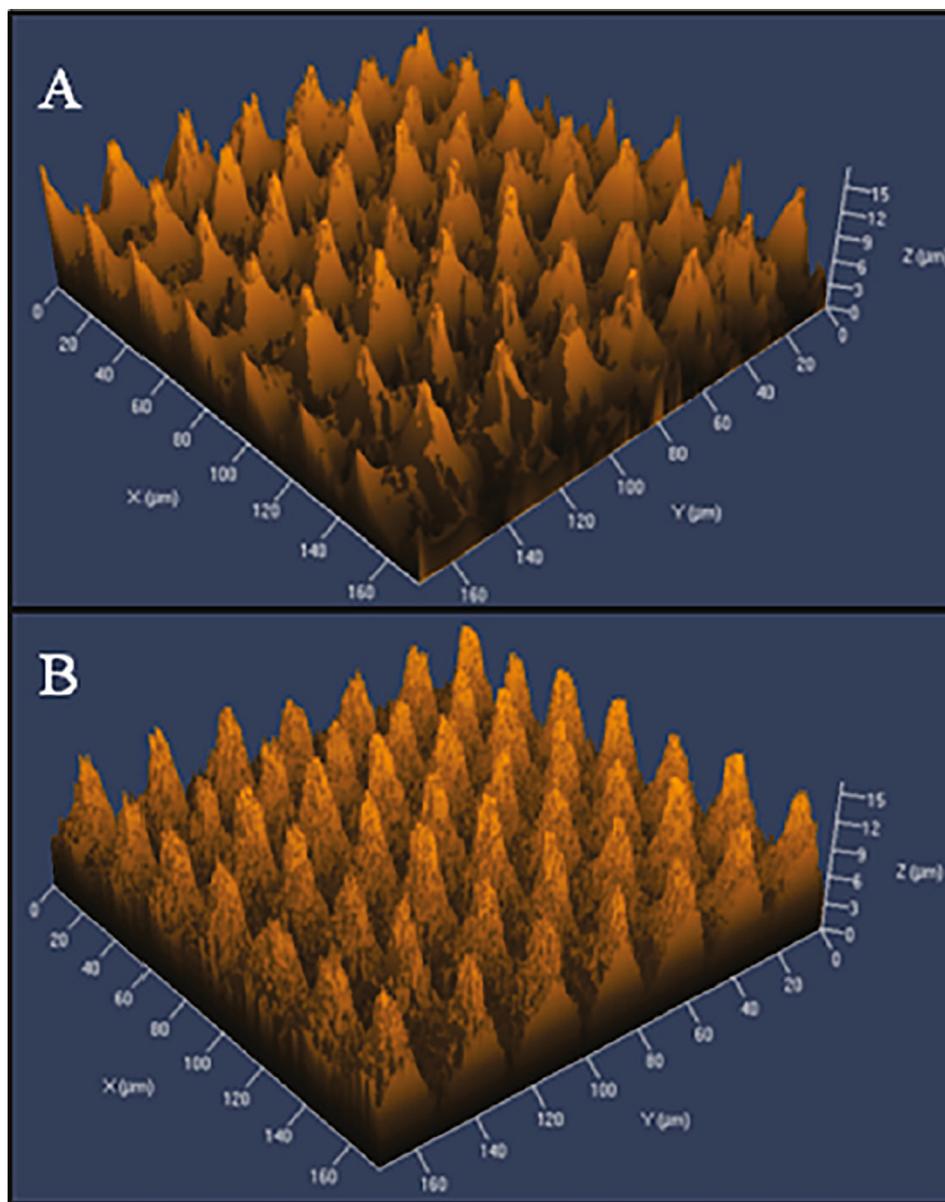


Fig. 16 – Confocal micrographs of laser ablation patterned Kapton HN (A) and PIS-1 (B) film samples. The laser ablation parameters for both images were 4.9 W and 80 kHz with a scan speed of 25.4 cm/s and 4 pattern transcription steps. At these settings, more material was removed from the Kapton HN surface compared to PIS-1, resulting in topography shape differences (pointed, concave conical features and conical structures with reduced concavity, respectively) (C) tilt and tap schematic for lunar dust simulant adhesion performance for lunar dust simulant was deposited by lightly agitating a simulant containing bottle positioned above the film. The sample was then tilted at 90° and tapped once on a hard, flat surface, and optical micrographs were collected on the resultant surfaces to observe the retention of simulant particles [14].

This self-assembly technique involves developing surfaces through the layer-by-layer coating, which enhances the stability and penetrability of the substrate. Zhao et al. [178] reported the combined layer-by-layer assembly for fabricating superhydrophobic surfaces using electrodeposition. Fig. 18 reveals the branchlike structure of silver nanoparticles. The tunable of the structures suggest the role of potential and time in achieving the multilayer as the porous structures can be

enhance by pH treatment. The as-prepared surface of the superhydrophobic revealed a water contact angle of 154°.

6. Applications of superhydrophobic ceramic based membranes for oil-water separation

Currently, a huge amount of oily wastewater is discharged to the environment as a result of production processes and

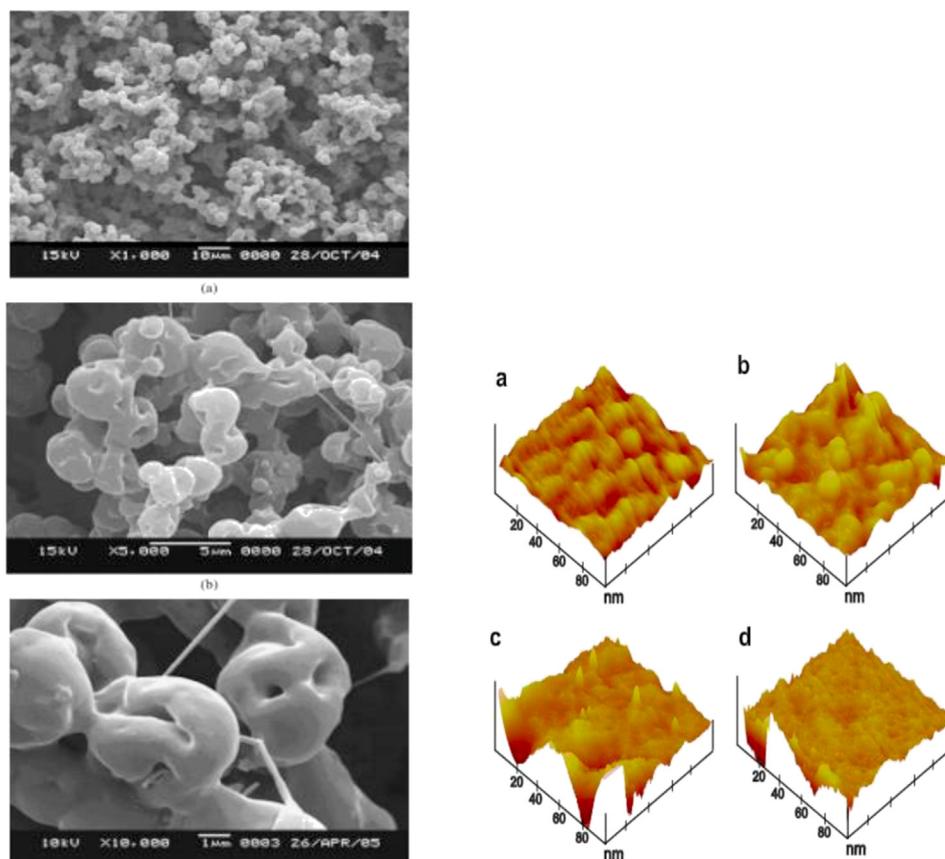


Fig. 17 – Left, SEM micrographs of electro spun PHBV film at different magnifications. The is film was electro spun from a 1.5 wt.% solution of PHBV in chloroform [15]. Right, AFM images of CTA fibrous materials with various plasma treatment times; (a) 0 s, (b) 60 s, (c) 180 s, and (d) 300 s.

frequent oil spillage accidents; this brings the attention of academia. Discharge of oily wastewater caused not only tremendous environmental issues but also caused uncountable economic losses. For this, there is a need for potential porous ceramic membranes with superhydrophobic-

superoleophilic features for separation of oil-water layered mixtures and oil-water emulsion. Superhydrophobic ceramic membrane can be able to disallow the penetration of water via the membrane but allow the passage of oil through the membrane as shown in Fig. 19. This concept could be used in

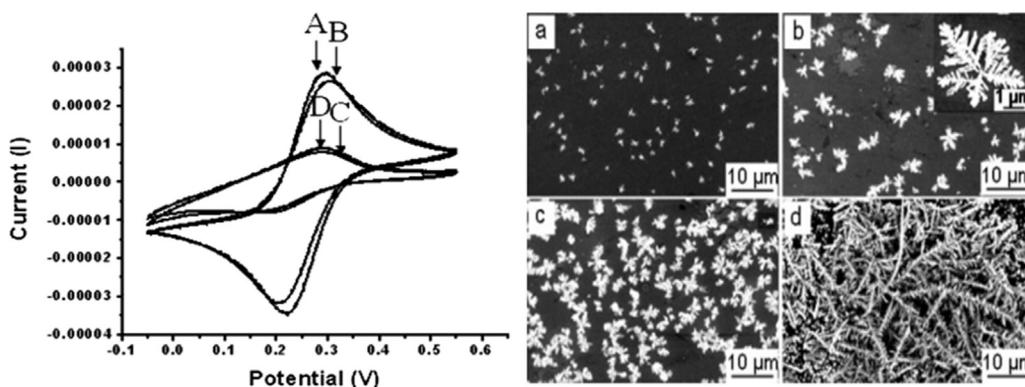


Fig. 18 – Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$, with a scan rate of 0.1 V/s, on (A) the bare Au electrode (B) the 3-mercaptopropionic acid modified Au electrode, and (C) the LbL modified Au electrode; all of them were taken after two cycles (D) Sample C taken after 100 cycles (E/V vs Ag/AgCl). SEM images of branchlike Ag aggregates formed on an ITO electrode modified with a polyelectrolyte multilayer by potentiostatic electrodeposition at -400 mV (vs Ag/AgNO₃). The deposition time is (a) 2 s, (b) 40 s, (c) 200 s, and (d) 1600 s. The image inset in panel b is the enlarged view of a Ag aggregate [16].

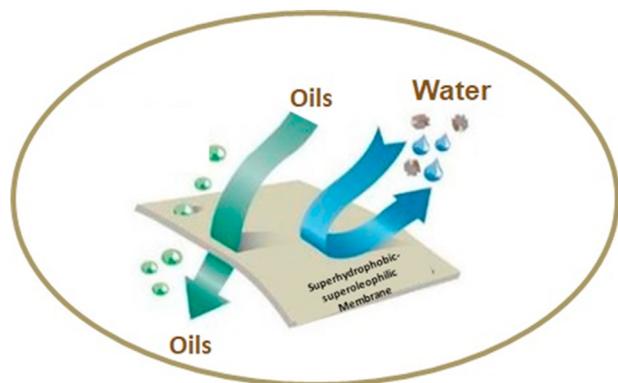


Fig. 19 – Superhydrophobic-Superoleophilic surface.

oil industries for recovering huge amount of oil from oilyw = wastewater in a much efficient way and high reclamation rate also, will provide greatly decrease the rate of fouling during the separation process.

Superhydrophobic-superoleophilic substrate can be used as an excellent wettability in the separation of oil-water mixtures which is achieved as a result of the difference in surface tension of water and oil. The oil-water mixture can be successfully be separated using the porous superhydrophobic-superoleophilic substrate thereby by selectively absorbing oil from the mixtures and at the same time completely repelling water. The first study on superhydrophobic-superoleophilic membrane for oil-water separation was reported by Feng et al. [179] they mimicked structural surface of lotus leaves by developing a Teflon coated stainless steel mesh using the spray and dry technique. Afterwards many researchers try to fabricate superhydrophobic-superoleophilic for oil-water separation using different substrates materials.

Ahmad et al. [180] synthesized superhydrophobic alumina ceramic membranes by direct grafting and sol–gel technique. They found that the alumina membrane grafted via the sol–gel method tends to have higher WCA of 158.4° as compared with the later method. The grafted membrane was able to reject 99.99% passage of water through the membrane

while recording higher kerosene flux of 117.160 ml/min during the filtration of kerosene and water mixture. Singh and Singh [181] fabricated superhydrophobic-superhydrophilic zirconia-based membranes for usage in oil-water separation. They used a hybrid mixture containing hexadecyltrimethoxy silane and steric acid as their agents of hydrophobic modification. The coated membrane shows WCA of 153°, sliding angle of 7° and oil contact angle (OCA) of 0°. It was reported that the modified membrane was able to effectively separate the sequence of the oil-water mixture with more than 99% efficiency even after 10 repeated cycles. The surface modification to fabricate superhydrophobic and superoleophilic alumina-based ceramic membrane for oil-water separation reported by Tang and co-workers [182] who fabricated a promising superhydrophobic alumina membrane with excellent superhydrophobicity and superoleophilicity of 155° and 0° respectively. The water rejection performance of the modified alumina membranes for oil-water separation is as high as 97% for 4 h. The authors claimed that the as-prepared alumina-based ceramic membrane has great potential for the separation of an oil-water mixture.

Hubadillah et al. [183] also successfully fabricated superhydrophobic-superoleophilic kaolin-based ceramic membranes for efficient absorption-separation of oil from water via organosilane silica sol–gel technique. The silane silica sol coating on the kaolin surface will simultaneously enhance the membrane surface roughness and at the same time lower the surface free energy of the membrane. The contact angle measurement was used to measure the hydrophobicity and oleophilicity of the membrane which was 157 and 0° respectively. In terms of the performance capability of the membrane, the grafted membrane was able to absorb almost 99% of oil through the membrane surface with a steady oil flux of 102 Lm⁻²h⁻¹. In another similar study, Jamaludin et al. [184] fabricated a facile superhydrophobic-superoleophilic ceramic membrane derived from sugarcane bagasse ash for oil-water separation. The grafted fabricated ceramic membrane shows promising features for oil absorption and water-repelling with an apparent contact angle of 163.9° and high oil-water separation efficiency of 99.9% with

Table 3 – Summary of various superhydrophobic ceramic membranes used for oil-water separation.

Precursor Material	Modifying Agent	Contact angle	Type of oil used	Oil Flux (L/m ² h)	Oil absorption capacity (g/g)	References
Kaolin ceramic membrane	Methyltrimethoxysilane (MTES)	161.3	Crude oil	80	10	[181]
Sepiolite	hexadecyltrimethoxysilane (HDTMS)	160	chloroform	–	7.2	[182]
Alumina ceramic membrane	Hexyltrimethoxysilane (HTMS)	140	kerosene	214.9	–	[183]
Porous ceramic tube	hydroxyl-terminated polydimethylsiloxane (HPMS)	161.2	kerosene	–	9.9	[160]
SiC membranes	Octyltriethoxysilane	167	hexane	1000	–	[184]
Halloysite nanotubes	Polydopamine/octadecylamine	156	trichloromethane	22.94	–	[185]
Janus ceramic membrane	hexadecyltrimethoxysilane (HDTMS)	160.8	Isooctane	955	–	[186]
Ceramic membrane	hexadecyltrimethoxysilane (HDTMS)	154	octane	99	–	[187]
Attapulgite membrane	Polydimethylsiloxane (PDMS)	151	Palm oil	2.9	–	[188]
Halloysite nanotubes	hexadecyltrimethoxysilane (HDTMS)	150	Chloroform	100	–	[189]
Alumina	Fluoroalkylsilane (FAS)	158.4	kerosene	117.16	–	[190]

oil flux of $137.2 \text{ Lm}^{-2}\text{h}^{-1}$. The studies also demonstrated that increase in grafting cycle would enhance the membrane hydrophobicity as a result of the formation of a more hierarchical structure of the grafting cycle conversely; increase in the calcination temperature will degrade the sol template embedded on the membrane surface resulting to decrease in the wettability of the grafted membranes. Suet al. [159] report a porous ceramic hollow fiber membrane with superhydrophobic/superoleophilic properties for oil recovery from oil water mixture. Water droplet shows a spherical shape on the modified membrane with contact angle of 161.2° . The porous ceramic membrane reported being able to directly recover oils from oily-water even if the feed contains solid particles. However, the velocity and separation efficiency of the modified porous membrane may be compromised by particle clogging and oil contamination. Table 3 below summarized the different superhydrophobic ceramic membrane developed for oil-water separation.

7. Conclusion and outlook

This review article provided an overview of the literature related to membrane separation technology, ceramic membrane fabrication processes and superhydrophobic surfaces. A detailed discussion on the current available preparation techniques and application status of superhydrophobic ceramic membrane for oil-water separation was provided. The merits and demerits of each surface modification technique were also identified. In general, it is known that oil molecules are prone to clog on hydrophilic ceramic membranes and lead to a decrease in the performance of the membrane. It is important to note that to achieve a superhydrophobic ceramic membranes surface with superior and lesser fouling tendency towards oily wastewater, the surface of the substrate plays a key role. The later can be obtained by various chemical modification processes. The chemical modification agents mostly used to prepare superhydrophobic ceramic membranes surfaces are organosilanes which are the most well-known chemical grafting agents. This is due to its appealing flexibility in coating superhydrophobic surfaces on a different type of substrates. The main principle of the grafting agent is to construct a suitable rough surface morphology that has low surface energy to render superb antiwetting properties for performance.

Although, the various methods of superhydrophobic fabrication have a great potential for separating oil-water mixture, but the stability of the hydrophobic ceramic membrane over a long period cannot be guarantee as the hydrophobicity of the membrane will be degraded with time. This is because the creation of a superhydrophobic ceramic membrane occurs on the outer surface of the membrane as such superhydrophobicity of the membrane will be lost if the membrane got eroded. For this, there is a need for accelerated investigation on full scale volumetric superhydrophobic membranes. Most of the fabricated superhydrophobic ceramic membranes reported are usually for laboratory or small-scale usage as they are only applicable to rigid or small flat surfaces; thus, this hinders the commercialization from being successful. Overall, more research should be pivoted

towards the use of cost-effective, environmentally friendly chemicals/raw materials for large scale fabrication of superhydrophobic ceramic membranes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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