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Fabrication of Biomimetic and Bioinspired Membranes

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Abstract

Biomimetic and bioinspired membranes are those membranes that are fabricated with natural or natural-like (inorganic, organic, or hybrid) materials via biomimetic and bioinspired approaches (bio-mineralization, bio-adhesion, self-assembly, etc.) to tailor-specific properties (sophisticated structures, hierarchical organizations, controlled selectivity, antifouling or self-cleaning properties, etc.). With the support of knowledge on mechanisms, models and functions from many scientific disciplines, research activity on biomimetic and bioinspired membrane during the last decade has increased rapidly.

Keywords: biomimetic, bioinspired, natural prototypes, membrane proteins, fabrication

1. Natural prototypes for bioinspired membranes

1.1. Cell membranes

Figure 1 illustrates the state-of-the-art examples that has shown great diversity of biomimetic and bioinspired membranes based on imitation of compositions (zwitterion and glycosyl), structures (biological channel), formations (biomineralization, bioadhesion, and self-assembly), and functions (self-cleaning) of the natural prototypes.

Among the natural prototypes, cell membranes are the most important due to their excellent abilities in mass transfer, energy transformation, and signal transduction. Cell membranes separate the cell interior from the outside environment and play a crucial role in almost all cellular phenomena. Each cell consists of $\sim 63,000 \mu\text{m}^2$ membrane area and a human body with 10^{14} cells that total to 10^7 m^2 of membrane area [1]. Cell membranes have a high degree of sophistication, miniaturization, and multi-functionalization. The present understanding of the cell membrane functions and complex membrane structures is primarily dependent on the fluid lipid bilayer and the proteins embedded within it (**Figure 2**). As such, cell

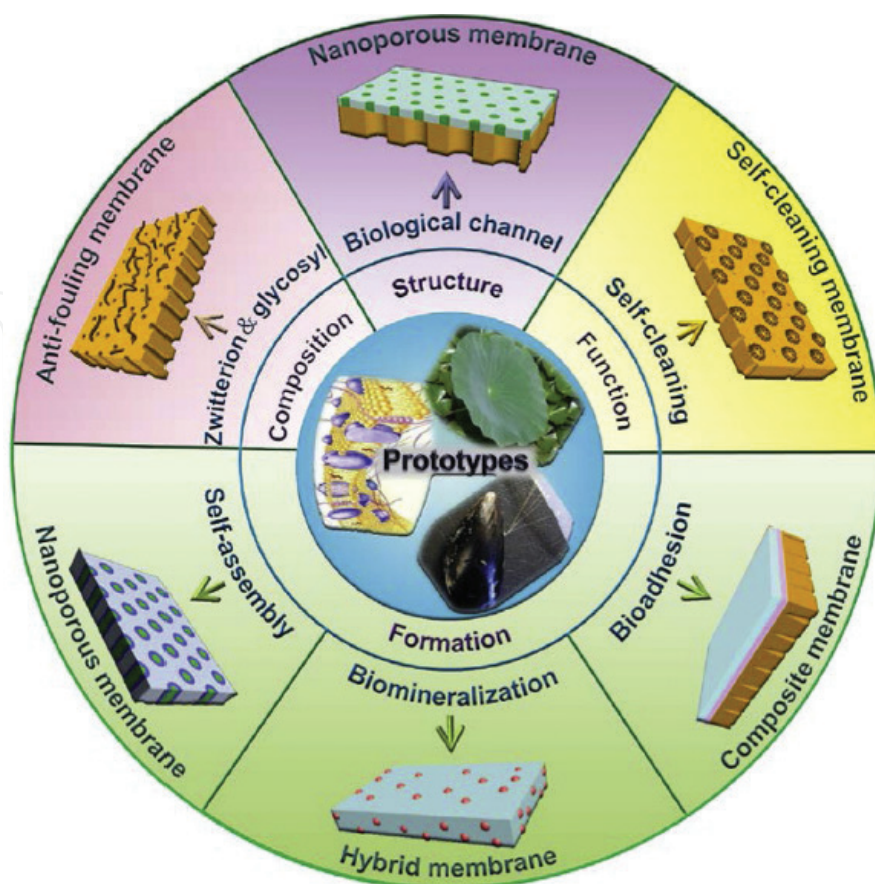


Figure 1. Overview of biomimetic and bioinspired membranes prepared by the imitation of natural prototypes.

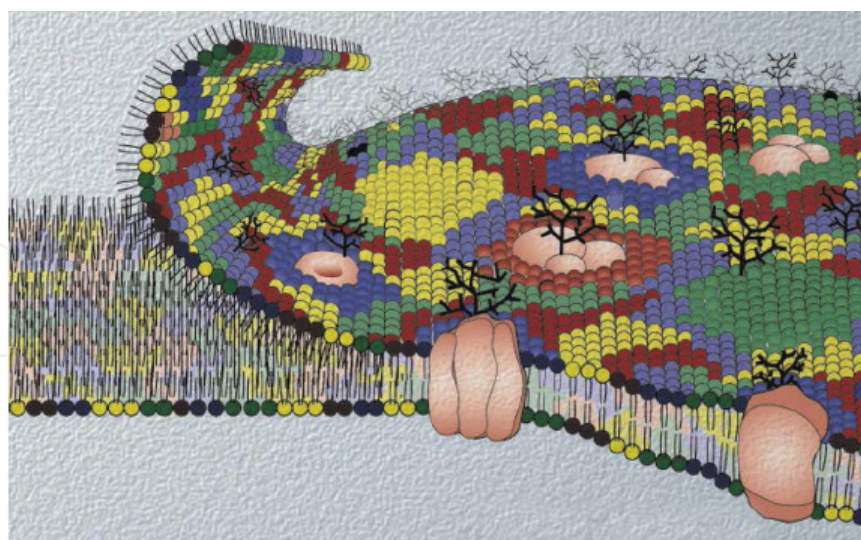


Figure 2. The fluid mosaic model with different lipid species shown in different colors. Source: Ref. [2], Copyright 2003; reproduced with permission from the Nature Publishing Group.

membranes are created using amphipathic lipids (phospholipids, cholesterol, glycolipids, and cholesterol esters), carbohydrates (oligosaccharides and polysaccharide), and membrane proteins (lipid anchored proteins, peripheral proteins, and integral proteins).

1.1.1. Lipid bilayer

The lipid bilayer is a universal component of all cell membranes. Its role is critical because its structural components provide the barrier that marks the boundaries of a cell. The structure is called a "lipid bilayer" because it is composed of *two* layers of *fat* cells organized in two sheets. The lipid bilayer is typically about five nanometers thick and surrounds all cells, providing the cell membrane structure.

Framed by the amphipathic nature of phospholipid molecules, the development of cell membranes occurs as a self-assembly type process. The phospholipids' nonpolar groups are included into planar bilayers with the aid of the hydrophobic effect. For instance, in a planar lipid bilayer, the nonpolar groups are mostly submerged into the bilayer's hydrophobic interior, while the polar head regions are positioned with respect to the external aqueous phase. Generally, the lipid bilayer is very fluidic and features assemblies of amphiphilic proteins (or lipoproteins) and lipids within the lipid's matrix. Furthermore, the interactions between the membrane lipids and exogenous proteins and peptides can incite a number of key biological processes at the level of the cell membrane [3]. As the primary phospholipid on the exterior surface, zwitterionic phosphatidylcholine shows superior nonfouling and nonthrombogenic qualities [3, 4]. This effective array of cell membranes offers excellent as well as rare instances of antifouling membranes' rational design.

1.1.2. Membrane proteins

Membrane proteins are proteins that interact with, or are part of, biological membranes. They include integral membrane proteins that are permanently anchored or part of the membrane and peripheral membrane proteins that are only temporarily attached to the lipid bilayer or to other integral proteins.

Cell membranes exhibit outstanding selectivity that allows certain substances permeating through them. Water as well as various smaller size molecules may move in and out of cells through active transport, facilitated diffusion, and direct diffusion. Small types of molecules, such as oxygen, water, ethanol, urea, and carbon dioxide, may easily move through cell membranes using simple diffusion mechanisms because of their higher solubility properties in the lipid bilayers' oily interior phase. These types of molecules move straight through the lipid bilayer or through the pores produced by essential membrane proteins. Alternatively, substances such as small organic molecules or ions move through cell membranes with the help of facilitated diffusion or active transport featuring protein-mediated carriers.

The facilitated or active diffusion is a diffusion using a carrier or channel proteins in the cell membrane that assists in the movement of molecules across a concentration gradient. All these processes play a crucial role in regulating the movement of solutes and water. The major intrinsic protein (MIP) is an important type of integral membrane proteins. MIPs are primarily divided as either aquaporins (AQPs) that can be only permeable to water or aquaglyceroporins (GLPs) that assist the diffusion of solutes like urea and glycerol [5]. As part of this, water channels have become the focus of a more rigorous research due to their effective transport mechanism. Specifically, there are several distinct water channel varieties. The AQP1 water channels permit water to travel bidirectionally and easily using osmosis across

cell membranes; however, this is not the case with other small inorganic and organic molecules as well as ions [6]. The overall rate of water transport through AQP1 (3×10^9 water molecules per sub-unit per second) is substantially higher than that of the channels [7]. The dynamic and crystallographic structures of AQP1 allow for a rapid water transport process. Experimental runs show that the AQP1 selectivity filter is relatively hydrophobic and covered with hydrophilic nodes, a series of six completely spanning α -helices and a junction of two shorter helices from the channel [8]. **Figure 3a** indicates the way in which partial charges from the helix dipoles constrain the positioning of the water molecules moving through the restricted area of the pore. The interactions between Asn 192 and Asn 76 amino acids hold this junction together and create a hydrophilic water gate that allows for the AQP1 selectivity. In this case, the water molecule's oxygen atoms construct hydrogen bonds with the amide groups (**Figure 3b**), while the assembling of the water's molecular orbital produces well-tuned water dipole rotation (**Figure 3c**). Furthermore, the overall diameter of the narrowest

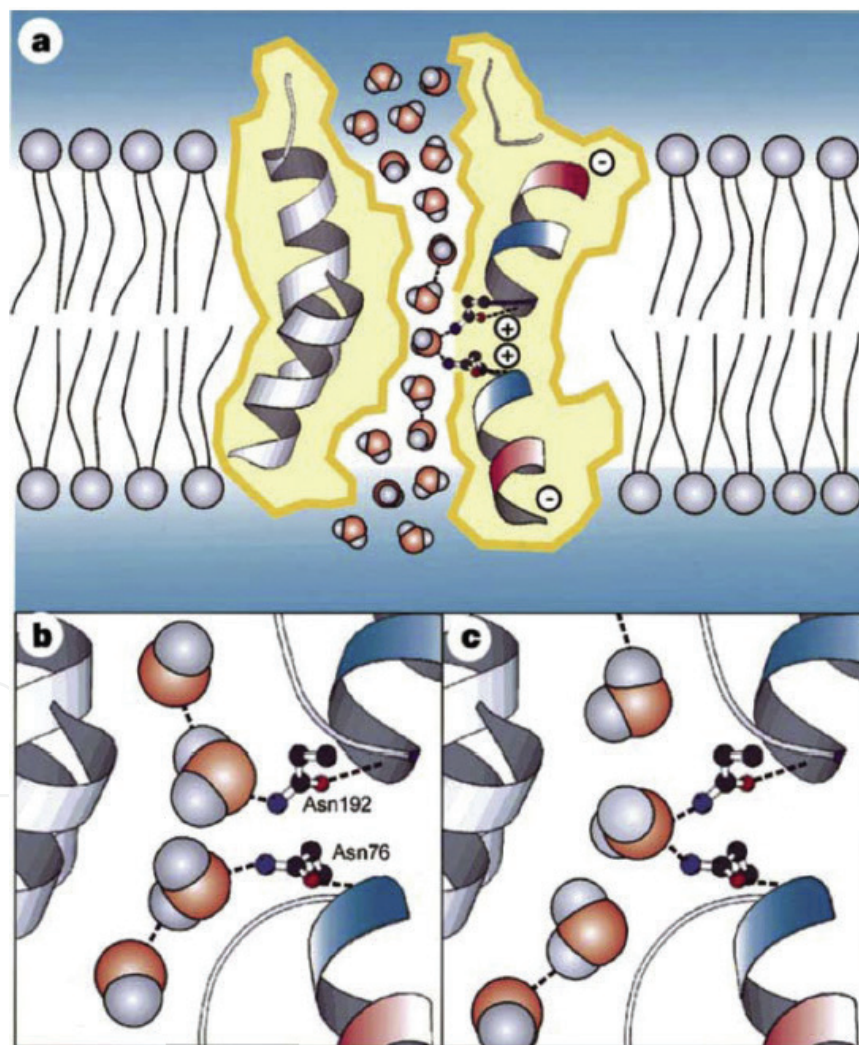


Figure 3. Schematic diagram of the water molecules transports in AQP1. (a) How partial charges from the helix dipoles restrict the orientation of the water molecules passing through the constriction of the pore. (b and c) The interactions and the hydrogen bonding of a water molecule with Asn 76 and/or Asn 192. Source: Ref. [9], Copyright 2000; reproduced with permission from the Nature Publishing Group.

point present is around 0.28 nm, and this likewise poses a steric obstacle for other molecules. The hydrophilic nodes, narrow size of the constriction region, and hydrophobic channel wall in combination contribute to the quick and accurate water molecule transport process [6].

The ion channels are a succession of pore-forming proteins that help control the voltage gradient throughout the membranes of living cells. Gating and selective ion conduction are two of the essential features attributed to ion channels. The selective ion conduction controls the performance of the channel, and how well it can choose specific ionic species among the available species in the cellular environment and then catalyze them using a prompt flow through [10]. Alternatively, the gating process controls the ion channel activity by being turned on and off. For instance, potassium (K^+) channels feature a selective filter close to the pore's extracellular side as well as a gate close to the intracellular side (**Figure 4**) [11, 12]. Whenever K^+ ion arrives into the selective filter, it is completely dehydrated. Such an unusual selectivity in K^+ channels is caused by the main chain atoms that have a stack of modified polar oxygen cages, which in turn allow for a series of closely spaced sites of appropriate dimensions to carefully arrange the process of K^+ ion dehydration. The hydrogen bonding and extensive van der Waals interactions ensure that the protein packing around the selective filter expands outward radially so as to keep the pore open at its appropriate diameter. Four helix dipoles and their electrostatic influence guarantee the cation selectivity by creating a negative electrostatic, or cation attractive, potentially close to the entry into the narrow selectivity filter [11]. The amino acid sequence preservation offers a frequent structural basis for the gating of K^+ channels, and the gating stimulus itself is caused by the membrane electric field and ligand binding [12].

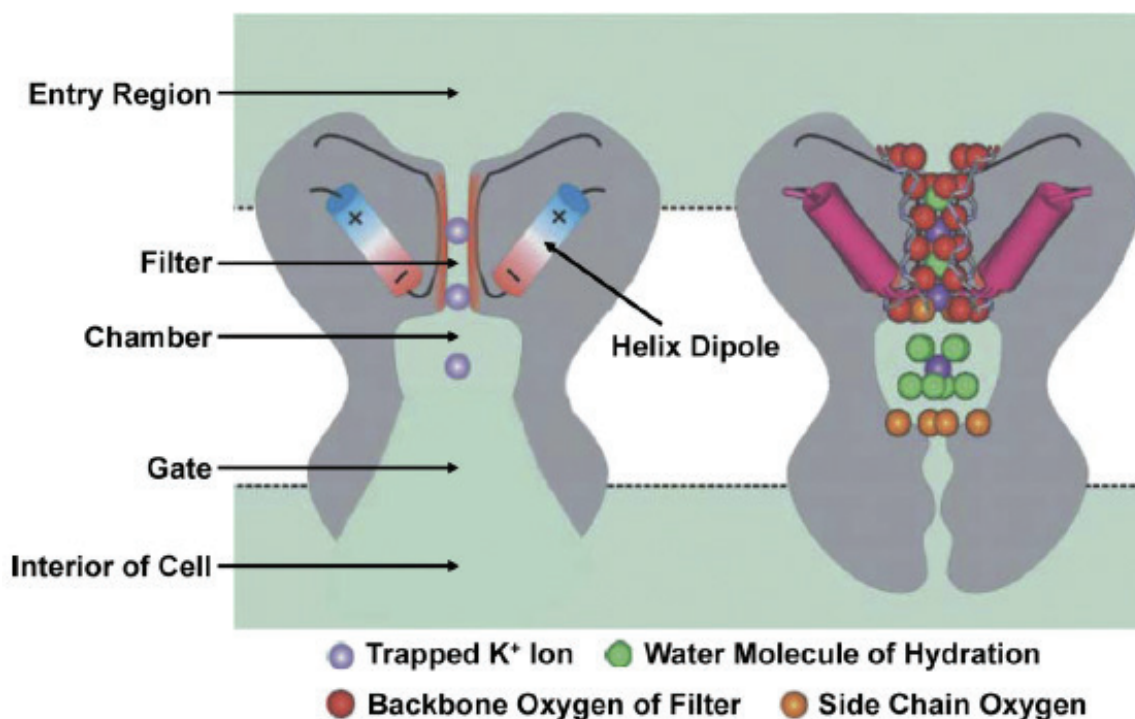


Figure 4. Cross-section of K^+ channels. (a) Wide open intracellular vestibule and pore helix dipoles; (b) high resolution structure for a closed channel. Source: Ref. [11], Copyright 2002; reproduced with permission from the Nature Publishing Group.

These delicate K^+ channel structures guarantee that K^+ ion is capable of diffusing from one site to the next within a relatively short distance. Moreover, it also restricts the accommodation of other ions or the rapid conduction within the high-selectivity dynamic. In nature, ion transport likewise happens with the aid of ion pumps. In terms of structure, the ion pumps are the large protein complexes that have their central channel portion spanning into the cell membrane [13]. Ion pumps are active transporters that are responsible for fulfilling a range of functions, unlike the ion channels that solely encourage the downhill movement of ions. The pumps effectively transport ions against their electrochemical gradient by coupling the “uphill” transport process with an energy source. An example of such a source can be found in the form of adenosine triphosphate (ATP) hydrolysis or the “downhill” movement of a substrate molecule or another ion [14]. A cell membrane and its functionality are one of the most effective designs available in nature. Cell design has inspired the creation of artificial as well as synthetic membranes with tailored structures, designed components, targeted performance, and specialized functions that offer a variety of applications in many fields. Applications like the complex lipid components and structures, multisubunit assemblies in cell membranes, and membrane proteins provide innovative solutions using new chemically and physically controlled mechanisms for artificial membrane designs requiring particular hierarchical structures and components. Uniquely advantageous cell membrane characteristics like self-healing, controllable permeability, and antifouling may offer promising directions in the use and exploration of artificial membranes [14].

1.2. Biomineralization

The concept of biomineralization shows how organisms can make hard materials in green and mild conditions. In particular, biomineralization stands for the mineral-formation process in organisms during which the inorganic elements collect on specific organics from the external surroundings and then form minerals under the modulating and inducing organics. The key feature of biomineralization is that biomolecules, such as polysaccharide protein and peptide, secreted by cells dictate the creation of minerals with a defined size, orientation, structure, and shape. This occurs because of the ordered collections of biomolecules and the interactions between inorganic and organic phases [15]. Living organisms are well known for utilizing minerals' material properties, when developing organic-inorganic hybrid materials for a range of applications [16]. In fact, in nature, biomineralization phenomena exist in each of the five major organism groups. So far, around 70 different types of biominerals have been classified, for example, calcium carbonate in the invertebrate skeletons, calcium phosphate in the bones and teeth of the vertebrate, iron oxide and iron sulfide in the magnetotactic bacteria, and the silica in diatoms [17]. Of these, the silicon-based and calcium-based minerals exist in the largest quantities, especially since calcium-based mineral accounts for about half of the biominerals [18]. If they are created under diverse circumstances, materials featuring identical chemical compositions may offer different morphologies. For example, calcium carbonate created in the leaves of plants is identified as amorphous, and the same calcium carbonate is calcite in the mollusk's shell [18]. **Figure 5** provides a rough overview of the roles that the organic and inorganic constituents have during the biomineral formation process. In most cases, insoluble organic matrix and inorganic mineral reactants are the key

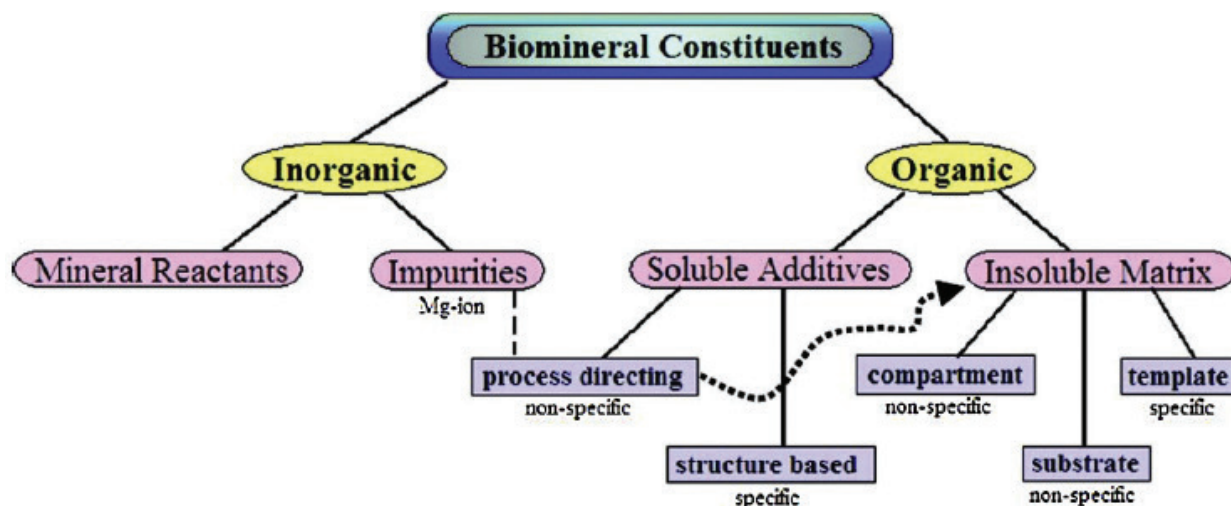


Figure 5. A simplistic view of the roles the inorganic and organic constituents played in biomineral formation process. Source: Ref. [19], Copyright 2008; reproduced with permission from the American Chemical Society.

factors, since the latter provides the necessary inorganic elements, and the former offers the substrate and functions as a template and an inducer of the mineral deposition. Furthermore, the crystallographic control can be regulated through the inclusion of organic additives and/or inorganic impurities. Although it is difficult to assess the intricate mechanisms leading to the formation of each biomineral, there are certain common strategies for manipulating mineralization. These strategies include spatial control, morphological control, structural control, constructional control, and chemical control [18]. Materials created using biomineralization in most cases have a substantially more complex structure and hierarchical organization than artificially synthesized materials. This ensures that they have improved physicochemical properties necessary for the molecular level control of organisms over the microstructure and nanobiominerals [20, 21]. For example, the ordered brick-and-mortar organization of CaCO_3 tablets and proteins in seashell nacre combines the strength of CaCO_3 together with the elasticity of proteins, thus ensuring that the seashell nacre exhibits strength, toughness, and hardness that exceed most manmade ceramics [22]. Furthermore, the physiological environment of the living organisms guarantees that the biominerals may be effectively synthesized in conditions that are environmentally friendly and mild, with almost neutral pH, aqueous environment, atmospheric pressure, and room temperature [23]. As a process, biomineralization joins superior properties, environmentally friendly conditions, and unique morphology, all of which are appealing features, when it comes to material synthesis. As a consequence, the idea of simulating biomineralization processes has remained an effective and promising methodology for synthesis and design of sophisticated organic-inorganic hybrid and inorganic materials using low energy and green approaches [24].

1.3. Bioadhesion

The area of bioadhesion stands for the ways in which natural materials adhere to a range of solid surfaces in a strong and quick manner. When it comes to natural phenomena, there are numerous examples of rare and exciting bioadhesion phenomena. This is particularly

applicable to marine organisms such as sandcastle worms, limpets, starfish, tube worms, giant clams, sea cucumbers, barnacles, kelp, and mussels. For example, marine mussels are capable of secreting adhesive proteins all along the ample threads fanning out from the sides of the shells and then terminating each thread from the external coating of the thread and the adhesive plaques [25]. Adhesive proteins can stick to solid surfaces and then harden during short periods of time in order to create a solidified layer in water. This process of solidification ensures that mussels may be firmly attached to almost any type of substrates, like rocks, ship hulls, and even wave prompt habitats [26, 27]. **Figure 6b** shows the attachment of mussels to glass using an adhesive system based on plaques and threads and called “beard” or “byssus.” Another relevant example is the sandcastle worm (*Phragmatopoma californica*) and its related species of marine polychaetes. These marine organisms can secrete cement from their “building organ” located on their thoraces, which allow them to glue particles such as shell fragments and sand grains together and then build a tube-like shelter [28, 29]. **Figure 6a** reflects the community of mussels fixed to rocks, and **Figure 6c** outlines the chemical formula embodying the byssus of mussel.

As **Figure 7** indicates that whenever a part of the worm’s tube is removed and if the building blocks like glass beads are available in abundance, the worm will carefully go through the gluing process in order to repair its tube section. Adhesive systems listed earlier have several key similarities, when it comes to composition. Research studies show that the mussels’ adhesive capabilities may be caused by the proteins located close to the plaque-substrate interface, like Mytilu edulisfoot protein 3 (Mefp-3) and Mefp-5, both of which contain sufficient 3,4-dihydroxy-l-phenylalanine (DOPA), with 21 and 27 mole%, respectively [26, 30, 31]. DOPA has a critical role in adhesive proteins, since it participates in the reactions that bring about the bulk adhesive proteins’ hardening. DOPA also helps to form durable noncovalent and covalent connections with substrates because of the chemically multifunctional characteristics of catechol groups in relation to DOPA [26]. Furthermore, metal ions in nonmineral forms are necessary for a range of bioadhesive processes. The iron-DOPA complexes are created in the byssus of the mussel (**Figure 6c**) and feature at least two important functions [25]. The first function allows to simultaneously enhance extensibility and solidity of the threads using the reversible formation of iron-DOPA bonds. The second, key function permits inducing the

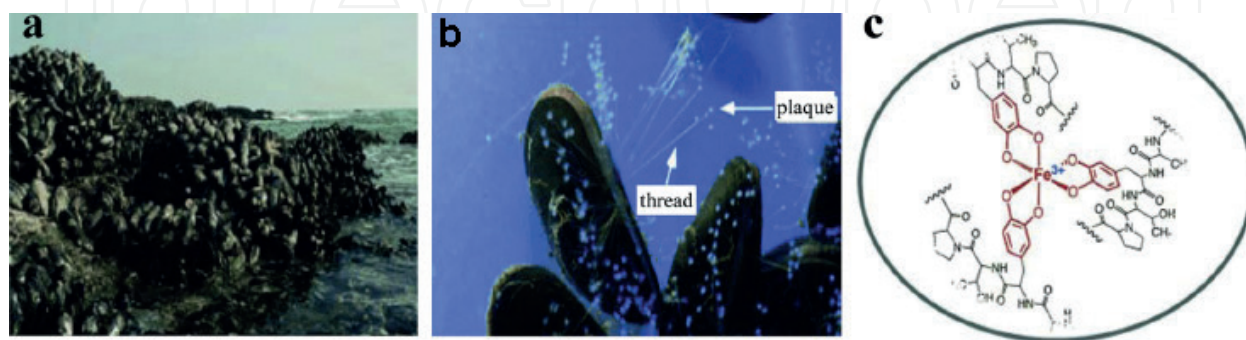


Figure 6. (a) A community of mussels affixed to rocks. (b) Mussels adhering to glass. The picture shows their byssus adhesive system consisting of threads and plaques. (c) An $[\text{Fe}(\text{DOPA})_3]$ complex. Source: Ref. [25], Copyright 2010; reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

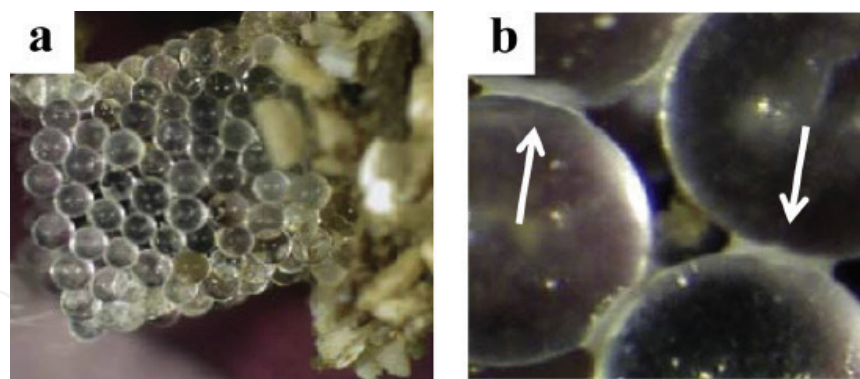


Figure 7. Sandcastle glue. (a) A tube rebuilt on top of the natural tube with 0.5 mm glass beads in the laboratory. (b) Close up of the rebuilt tube. Source: Ref. [29], Copyright 2011; reproduced with permission from Elsevier Ltd.

oxidation and the following DOPA reactions, which in turn helps to achieve the creation of the adhesive plaques and outer coating of threads. When comparing them to various synthetic adhesives, bioadhesives offer substantially more gains, such as durability, superior strength, quicker formation process, nontoxicity, milder formation conditions, and universality [25, 30]. In addition, all the bioadhesion processes occurring in living organisms happen in the presence of water, while underwater adhesion has been a constant roadblock for the majority of man-made types of adhesives. As a result, bioadhesion phenomena and the mechanisms they use have drawn a lot of attention in the last decade. Some researchers have tried to synthesize or screen models analogous to bioadhesives by simulating their properties and constitutions, since substantial difficulties arise in relation to the costs and processes of obtaining purified natural bioadhesives. For example, dopamine (DA) has been commonly used as an adhesive because of its similar properties and structure resembling DOPA [32, 33]. The growing research area of bioadhesion mechanisms has been exploring new innovative directions, including biomimetic adhesion strategies that can have extensive applications in the development and design of composite membranes with robust interfaces and uses [34].

1.4. Self-assembly

The phenomenon of self-assembly conveys the way in which organisms can create a wide range of complex structures featuring a high level of intricacy and precision. The definition of self-assembly is that it is a process of spontaneous organization of molecules in specific thermodynamic equilibrium conditions and into well-defined structural arrangements. In nature, there are a number of ingenious designs for structurally compatible and chemically complementary constituents capable of molecular self-assembly. Examples of these include deoxyribonucleic acid/ribonucleic acid DNA/RNA, polysaccharides, and peptide/proteins. The degree of ubiquity of the self-assembly phenomenon which occurs in nature, at either macroscopic or microscopic scales, reflects the capacity to spontaneously combine different individual entities into well-defined structures and cohesive organizations using nonspecific as well as specific intra/intermolecular relations [35, 36]. The cell membrane and its structure is one such characteristic example of molecular self-assembly occurring in nature. The lipid bilayer configuration has the capacity to show complex morphological changes using the

phospholipids assembly. For instance, primitive cells can sustain the basic cellular functions such as division and growth with the help of lipid assembly [37]. The lipid bilayer likewise has a key role in the organization and assembly of amphiphilic transmembrane proteins, since they are guided by hydrophobic, or hydrophilic, interactions. Natural proteins and peptides may self-assemble into ordered molecules due to their evolutionarily fine-tuned functions and unique structures. A widely known instance of this occurs in the spider silk, which is famous for remarkable flexibility and strength [38]. Spiders are capable of manufacturing different types of spider silks using amphiphilic silk proteins, or spidroins, that have repetitive hydrophobic and hydrophilic amino acid stretches bordered by carboxy terminal and conserving nonrepetitive (NR) amino-terminal regions [39–41]. In this case, the assembling of charged N-terminal domain may be controlled with the aid of pH, since the pH gradient of spider silk glands can help to regulate the silk formation process. Next, the C-terminal domain, which is indifferent to pH changes, can regulate silk formation process by ordering the assembly of repetitive segments into actual fibers [39, 40]. The larger hydrophilic NR terminal regions make these silk protein molecules surfactant-like and make sure that they have the capacity to form micelles or hexagonal columns. This is followed by larger globular structures that are elongated due to the changes in their shear forces and extensional flow, thus creating the precursors to the subsequently produced spider silk fibers (**Figure 8**) [42]. As a common characteristic of extracellular organic matrix macromolecules, self-assembly depends on specific intermolecular interactions. In fact, the formation process of natural inorganic-organic composites begins with the careful assembly of extracellular matrix, then followed by selective transportation of inorganic ions to the organized compartments, subsequent mineral nucleation, and, finally, to the mineral growth defined by the confined cellular compartments [43–45]. As a consequence, the process of self-assembly in protein scaffolds has a vital role when it comes to the composite seashells' rich diversity [46]. Self-assembly

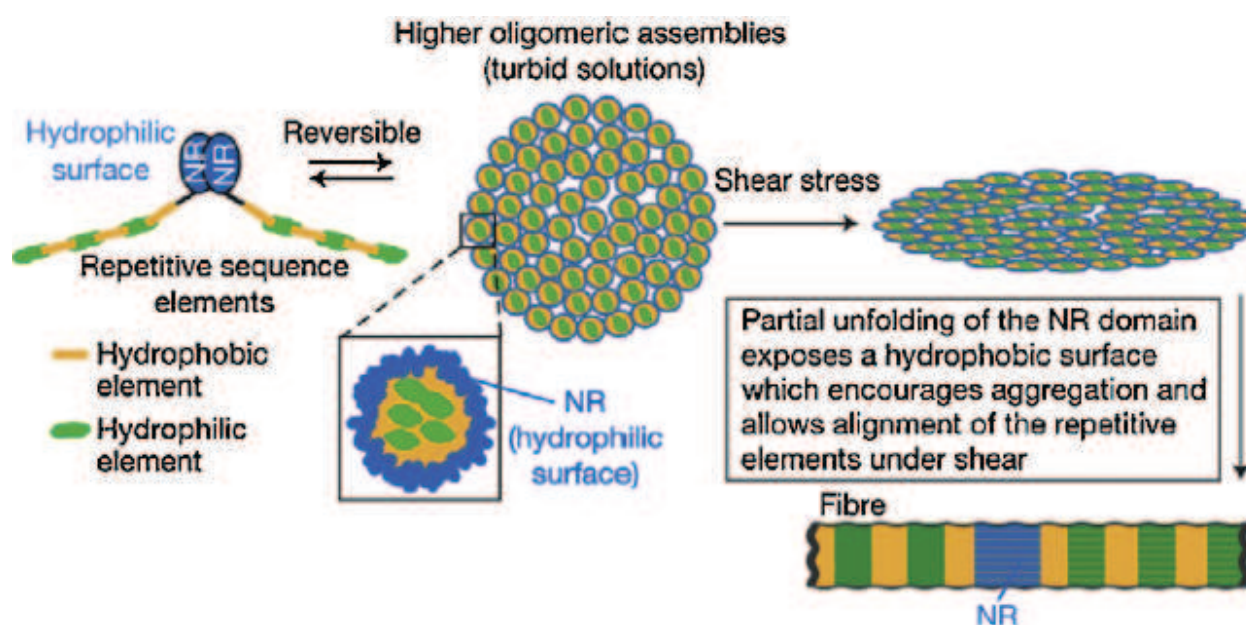


Figure 8. High oligomeric assemblies from silk proteins. Source: Ref. [39], Copyright 2010; reproduced with permission from the Nature Publishing Group.

has been proposed as an intelligent and bioinspired strategy for producing membranes with controlled architecture and composition and highlighted for incorporating a variety of building blocks into artificial/synthetic membranes.

1.5. Self-cleaning

The phenomenon of self-cleaning reflects how the surfaces of an organism can show a low-adhesion potential for a wide range of foulants occurring during the fluid flow. The qualities of biological surfaces, ranging from interplay between chemistries to surface morphologies, have a key role when it comes in defining specific wettability of biological materials. For example, superhydrophobic nonwetting quality is an essential property of standard self-cleaning biological surfaces. In the case of plants, this self-cleaning phenomenon is generally referred to as the “Lotus effect”. Drops of water accumulated on the lotus leaves bead up when experiencing a high contact angle and then roll off, collecting dirt along the way in a mechanism of self-cleaning [47]. Plant surface nanostructures and microstructures play an intrinsic role in self-cleaning processes. Certain plant surfaces become hyper self-cleaning and hydrophobic because of the hydrophobic epicuticular waxes and hierarchical roughness. As one of the typical biological objects, the lotus leaf is well known for the combinatory use of hydrophobic epicuticular wax and the micro/nanoscale hierarchical architectures on its surface [48, 49]. In this case, the first structure is made out of microlevel mound-like protrusions featuring papillose epidermal cells, while the second structure is made out of nanoscale branch-like growths happening in the epidermal cells (**Figure 9a** and **b**) [50, 52]. This hierarchical roughness produced by randomly oriented hydrophobic wax tubules and convex cell papillae is essential for the preservation of the lotus leaf’s self-cleaning characteristics (**Figure 9c**) [51, 53]. Particles contaminating the lotus leaves are picked up by the water droplets and then removed as the droplets slide off [54]. Plant surfaces tend to appear as rather diversified types of surface structures, as indicated in **Figure 10**. Distinct structures in two scales are helpful for lowering surface energy, forming the self-cleaning surfaces, and trapping air [57]. Furthermore, the physical adhesion forces that exist between the structured surfaces and contaminating particles can be significantly reduced. Within the realm of nature, self-cleaning processes and

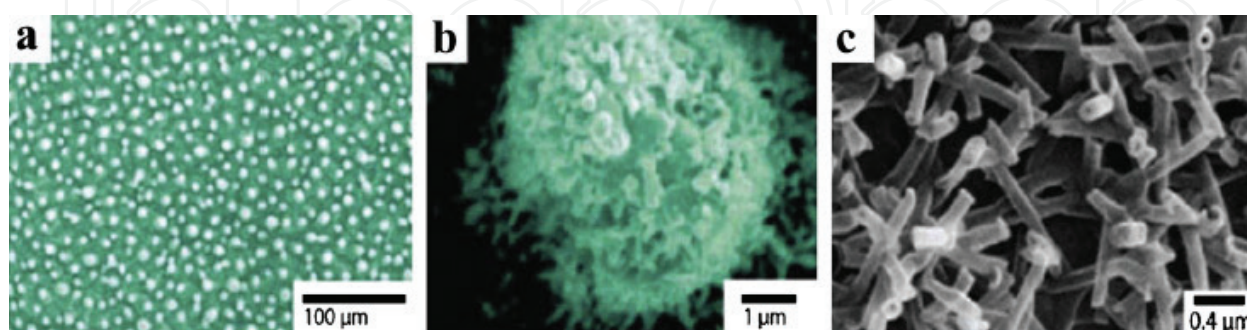


Figure 9. (a) Large-area SEM image of the lotus leaf’s surface. Every epidermal cell creates a papilla and has a dense layer of epicuticular waxes superimposed on it. (b) Enlarged overview of a single papilla from panel [50]. (c) SEM image of 3D epicuticular wax tubules on lotus leaf surfaces, which create nanostructures [51]. Source: Refs. [50, 51], Copyright 2002 and 2009; reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA and the American Chemical Society, respectively.

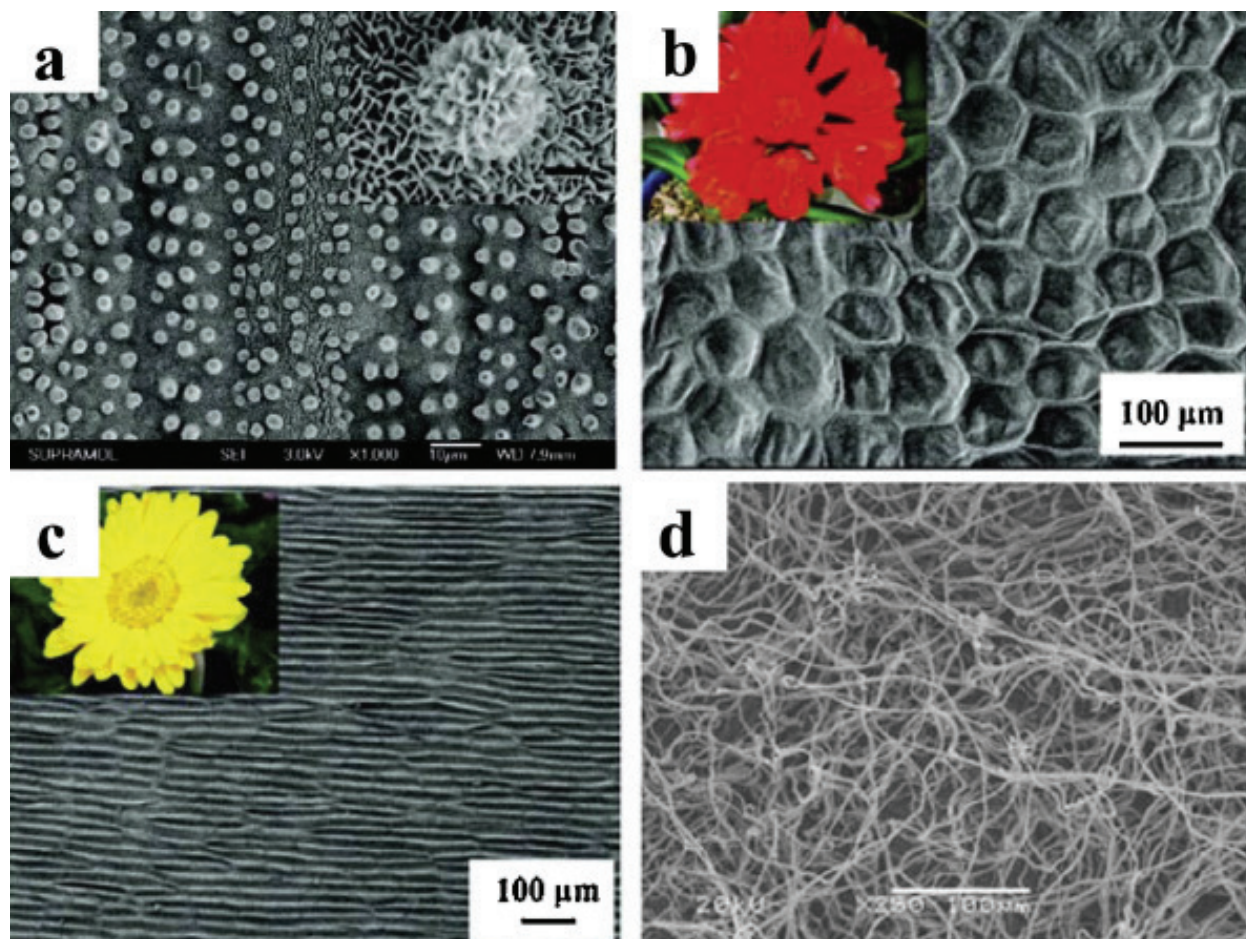


Figure 10. SEM images of the surface of (a) hierarchically structured papillae arranged in quasi-one-dimensional order parallel to the leaf edge [55], (b) periodic array of close-packed hexagons and strips on Chinese Kafir lily petal [56], (c) periodic array of parallel lines and helices on sunflower petal [56], and (d) unitary web of micro-fibers on ramee rear face [57]. Source: Refs. [55–57], Copyright 2010, 2008, and 2007; reproduced with permission from the American Chemical Society and Elsevier Ltd., respectively.

mechanisms are not limited only to plant surfaces. A wide range of self-cleaning surfaces have likewise been identified in water strider legs, insect eyes, insect wings, shark skin, gecko feet, spider silks, bird feathers, fish scales, and other types of surfaces [49, 58].

In the case of the Morpho butterfly wings, multiscale as well as ordered photonic structures improve self-cleaning and superhydrophobicity characteristics (**Figure 11**) [59, 60]. This directional easy-cleaning quality of the Morpho butterfly wings can be explained by its unique direction-dependent alignment of flexible nanotips on top of the lamella-stacked nanostructures and microscales overlapped on top of the wings [61]. Another example is found in gecko's feet, as they can engage in the process of self-cleaning, while the walking occurs with sticky toes. This exciting self-cleaning quality can be caused by the nanostructure, or single seta with a branched structure terminating in hundreds of spatula tips, and microstructure, that is setae on overlapping lamellar pads in uniform arrays. It seems that nonadhered lamellar surfaces can be quite nonwettable, and the particles contacting unloaded surface would be easily washed away when water becomes present. Furthermore, gecko feet that have been contaminated with microspheres may likewise retrieve their capacity to cling after a few steps on a dry

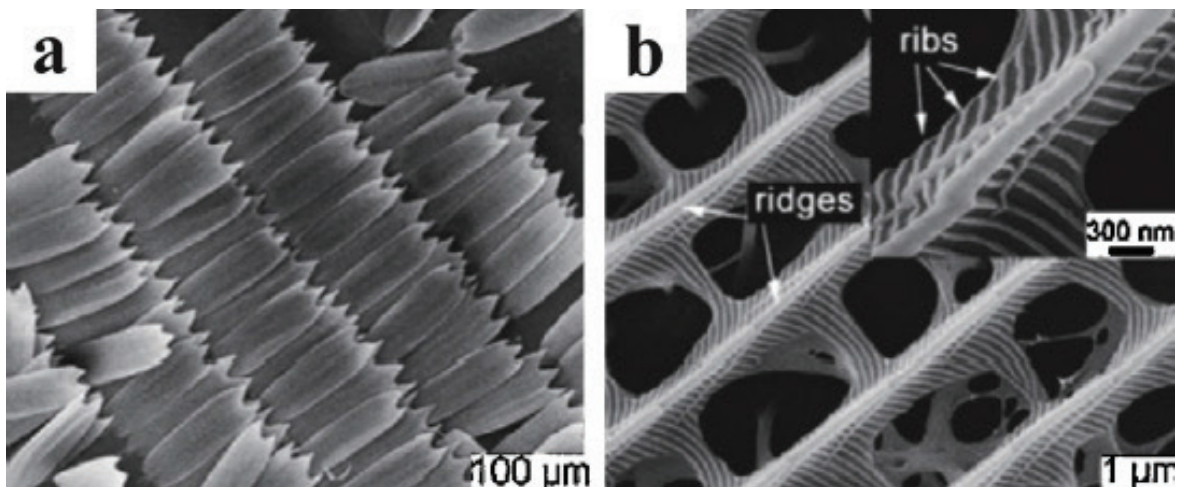


Figure 11. Hierarchical microstructures and nanostructures on the surface of the Morpho butterfly wings. (a) Secondary electron image of overlapping scales possesses an overall rectangular shape with pointed tips. (b) Secondary electron image of the porous architecture of the scale with parallel microscale ridges aligning along the scale length and nanoscale ribs lying on each ridge. Source: Ref. [59], Copyright 2008; reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

surface, such as the one offered by clean glass. The process of self-cleaning is a consequence of the energetic disequilibrium that occurs between the adhesive forces that attract a dirt particle to the substrate, and those that attract the same particle to one or more spatula [62, 63].

In addition to the superior hydrophobic surfaces that occur in the air, nature likewise produces low adhesive surfaces in water environments. Examples of these adhesive surfaces that act as an inspiration for developing underwater self-cleaning surfaces are the surfaces of fish made up of tough scales and hydrophilic flexible mucus. The sector-like carp scales are created by orienting micropapillae with nanostructures of 30–40 μm in width and 100–300 μm in length and assembled in a radial direction (**Figure 12**) [63]. Whenever such fish scales come

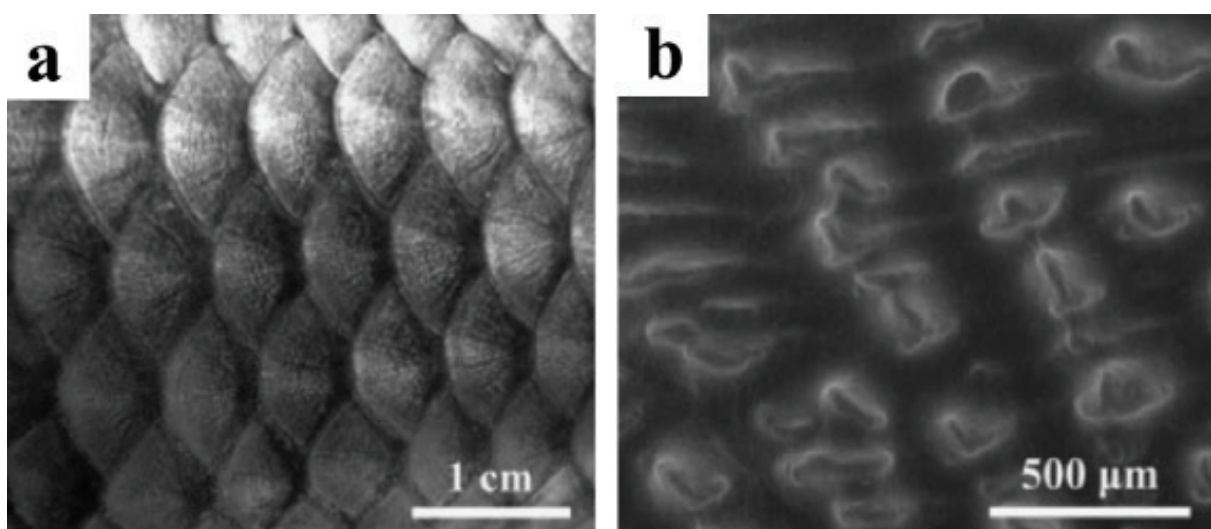


Figure 12. Surface structures of fish scales: (a) Optical image of the fish scales. (b) SEM image of fish scales. Source: Ref. [64], Copyright 2009; reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

in contact with something like oil droplets in water, their fine-scale hierarchical structures can secure water molecules and then create an oil/water/solid interface. Further illustration of the underwater self-cleaning surface can be found in shark skin, which is protected by rather small separate tooth-like dermal denticles ribbed with longitudinal grooves. When these grooved scales are aligned parallel to the local water's flow direction, they can significantly reduce the creation of vortices over the smooth skin surface, thus enhancing water movement and flow efficiency [65]. To sum up, both, the microstructures and nanostructures, and the chemical properties of biological surfaces are capable of deterring contaminant matter from the surface and may offer an innovative direction for the construction of bioinspired and biomimetic self-cleaning membrane surfaces.

2. Synthesis of bioinspired and biomimetic membranes

Nature has always found a way to evolve common materials with functions that stand out as desirable. In fact, nature's sophisticated methods of selection have inspired advanced research directions in membrane materials and production. Biological structures, functions, formations, and compositions tend to take their forms on multiple scales ranging from molecular to microscale, macroscale, and nanoscale and in a manner that is strategically hierarchical and makes up a range of key functional elements. This exciting bioinspired and biomimetic trait has been especially appealing when it comes to designing and producing new synthetic membranes with superior structures, formations, functions, and compositions. The concise overviews of the six types of bioinspired and biomimetic membranes and their corresponding natural prototypes are covered in this review and are outlined in **Table 1**.

2.1. Fabrication of biomimetic and bioinspired membranes based on compositions of natural prototypes

2.1.1. *Based on zwitterion and glycosyl*

2.1.1.1. *Fabrication of membranes via surface zwitterionization*

Zwitterions are based on compounds that have an equal number of negatively and positively charged groups and, as a result, show an apparent neutral state. Research shows that there are biological zwitterionic phospholipids on the external lipid layer of the cell membrane. They are there to enhance biocompatibility with the surrounding tissues and stop the adhesion of exterior matters in biological fluids [4]. When it comes to bioinspired and biomimetic membranes, a variety of zwitterionic compounds have been used for the process of membrane surface zwitterionization. Because of the enhanced zwitterionic head group's fouling resistant qualities in cell membranes, the aim of surface zwitterionization is to stop foulants from attaching themselves to the membrane's surface. Research has shown that a number of typical zwitterionic moieties have been effectively introduced onto the surface of the membrane. A robust hydration of the zwitterionic moieties can create a sturdy hydration layer on the membrane's surfaces with the aid of electrostatic interactions that provide membranes with good fouling resistant abilities

Classifications	Natural prototypes	Biomimetic and bioinspired membranes
Based on composition	<i>Zwitterion and glycosyl</i> : the functional groups on the outside of cell membrane which renders antifouling properties	Antifouling membranes with functionalized surfaces resembling the composition of cell membrane through surface zwitterionization and glycosylation
Based on structure	<i>Biological channel</i> : the transmembrane proteins or protein assemblies which provide the fastest and specific transport channels for ions and small molecules <i>via</i> passive transport	Nanoporous membranes with ordered transport channels for ions and small molecules through incorporating biological channel proteins and/or artificial nanochannels
Based on formation	<i>Biomineralization</i> : the formation process of biominerals in organisms through precise hierarchical assembly of nanoscale building blocks under regulation of biomolecules	Organic-inorganic hybrid membranes with inorganic nanoparticles formed within polymeric matrix through the <i>in situ</i> mineralization reaction of inorganic precursors under the inducing and modulating of organics
	<i>Bioadhesion</i> : the high-strength conglutination of organisms (especially marine organisms) onto solid surfaces under mild condition and aqueous environment through the combination of multiple interactions	Composite membranes with high interfacial strength between different layers or different moieties through incorporating biomimetic adhesion strategy to form multiple interactions on interfaces
	<i>Self-assembly</i> : the spontaneous organization of molecules under thermodynamic equilibrium conditions into structurally well-defined arrangements based on numerous specific and nonspecific intermolecular/ intramolecular interactions	Nanoporous membranes with ordered channels through self-assembly of block copolymers; nanoporous membranes with hydrophilic surface through self-assembly and spontaneous segregation of amphiphilic copolymer (surface segregation)
Based on function	<i>Self-cleaning</i> : the capacity of some biological surfaces to clear dirt away and keep themselves clean due to their superhydrophobic and nonwetting attributes	Self-cleaning membranes with superhydrophobic or superhydrophilic/oleophobicity surfaces through incorporating low surface energy moieties or high hydration energy moieties

Table 1. Introduction of natural prototypes and the corresponding biomimetic and bioinspired membranes [65].

and superior hydrophilicity [66]. The process of grafting zwitterionic moieties onto the surface of the membrane allows for an effectual method of realizing surface zwitterionization using covalent bonding. This method has received a lot of attention because of its potential applications. Different types of chemical reactions were engaged so as to fixate the zwitterionic moieties onto membrane's surface after it was formed. Graft polymerization offers an appealing route for membrane surface modification processes because of the monomer species' diverse range. The high-energy radiation-initiated graft polymerization process has gained considerable attention as one of the conventional methods for grafting functional polymer brushes from membrane surfaces and with the aid of which radiation-grafted zwitterionic brushes can be obtained using straightforward control. With the aid of the UV-irradiated technique and plasma pre-treatment, surface zwitterionization applied using graft polymerization of the zwitterionic monomer on the hydrophobic surface of poly(vinylidene fluoride) (PVDF) microfiltration (MF) membrane, polypropylene MF or nonwoven fabric membrane [67–70], polytetrafluoroethylene (PTFE) MF membrane, and polyethersulfone (PES) ultrafiltration (UF) membranes and polysulfone (PSf) UF membranes [71–74]. It should be noted that the high-energy types of excitation could likewise

create unwanted branched, or cross-linked brush structure, as well as photo degradation of the substrate membrane [75]. Alternatively, chemically initiated graft polymerization is moderate and does not need special equipment. Zwitterionic SBMA and CBMA monomers were grafted using the surface of PVDF membranes and physisorbed free radical grafting methods that rely on azo-bis-isobutyronitrile (AIBN) as the initiator [76, 77]. In addition, the process of grafting the zwitterionic MPC and MPDSAHA monomers from hydroxyl-containing membrane surface was similarly conducted with the aid of ceric ammonium nitrate, which was applied as a redox initiator in an aqueous medium [78, 79]. Numerous challenges still exist for the uniform zwitterionic brushes and high-grafting densities because of the steric effect of the monomers that have been already grafted. In the last decade, surface-initiated controlled radical polymerization, such as the surface-initiated reversible addition-fragmentation chain transfer polymerization (SI-RAFT) and surface-initiated atom-transfer radical polymerization (SI-ATRP), has been frequently used to create well-defined zwitterionic brushes on the membranes' surfaces. The process of surface zwitterionization based on surface-initiated controlled radical polymerization was applied extensively, and a mixture of various anionic and cationic pairs ($N^+(CH_3)_2/SO_3^-$, $N^+(CH_3)_2/COO^-$, $N^+(CH_3)_2/PO_4^-$) has been created so as to ensure the overall charge neutrality and high-membrane hydrophilicity [80]. In recent projects, the application of click chemistry, or the generation of products that follows nature's examples, for specific surface modification processes has offered a new route for membrane surface zwitterionization. This innovative direction features good control, high yield, and mild reaction dynamic. The surface attachment of long-chain and short-chain zwitterionic moieties has been obtained with the help of azide-alkyne cycloaddition reactions and surface-initiated thiolene coupling chemistry [81, 82]. The physical adsorbing and blending of zwitterionic copolymers with membrane-forming polymers are easier approaches to surface zwitterionization. Although zwitterionic brushes possess the high water affinity qualities, a number of amphiphilic zwitterionic copolymers were first synthesized and then implemented so as to augment the overall stability of zwitterionic brushes with the mediation of hydrophobic interaction occurring between the membrane's matrix and hydrophobic chains. While the membrane preparation process by in situ blending was occurring, the amphiphilic zwitterionic copolymers may stimulate surface separation of zwitterionic brushes onto the membrane's surface with hydrophobic chains fastened in the membrane's matrix [83]. Throughout the membrane's process of modification, the amphiphilic zwitterionic copolymers may be adsorbed on the membrane's surfaces and with hydrophobic chains fastened to them [84]. Once the expansion of surface modification methods has begun, new exciting chemical reactions and techniques are being used for the construction of composite zwitterionic membrane surfaces. These techniques include oxidative polymerization of zwitterionic amino acid 3,4-dihydroxy-L-phenylalanine (DOPA) and initiated chemical vapor deposition of zwitterionic polymers, chemical crosslinking of zwitterionic colloid particles, and interfacial polymerization of zwitterionic amide monomer [85]. The process of membrane surface zwitterionization may likewise result from membranes that include pyridine or N,N-dimethylamino-2-ethylmethacrylate (DMAEMA) moieties, featuring tertiary amine reactive sites [86].

2.1.1.2. Fabrication of membranes using surface glycosylation

A sufficiently hydrated glycocalyx (glycoprotein-polysaccharide) is located on the outside of the cell membrane and helps to manage specific interactions, like cell-cell recognition, as

well as stop unwelcome nonspecific protein adhesion through a mixture of hydrogen bond indicated hydration and steric repulsion effects. When it comes to bioinspired and biomimetic membranes, certain glycolmonomers or glycopolymers are implemented as biomimetic materials for the process of membrane surface glycosylation. Due to the fouling resistant quality of glycocalyx on the membrane's surfaces and the glycoside cluster effect, the aims of surface glycosylation are the identification of proteins or the deterrence of nonspecific interactions between proteins and membrane surfaces through the production of extended hydroxyl group rich chains enclosed by molecules of water.

2.1.2. Shortcomings and challenges

While in-depth research has been conducted on glycosylation and membrane surface zwitterionization, the majority of the tests were limited to the lab scale. First of all, the scale-up of complex polymer modification and synthesis strategies is problematized by reaction conditions' precision control, including the control of temperature, residence-time, velocity, and catalyst distribution in the reactor. Second, zwitterionic moieties are frequently too costly to implement in larger quantities. In addition, glucosyl moieties may be susceptible to microbial degradation during the repeated and long-term application. Finally, the comprehensive knowledge of the membrane's structural evolution under varying condition has not been fully investigated. However, glycosylation and membrane surface zwitterionization offer the most encouraging directions in environmental, engineering, and biotechnical applications of innovative membrane technologies [87].

2.2. Fabrication of bioinspired and biomimetic membranes based on structures of natural prototypes

2.2.1. Biological channel structure

There is a substantial number of channels formed by proteins, as well as protein assemblies, within the cell's membrane and that effectively contribute to the transmembrane transport of water, nutrients, and ions [6, 87]. The rapid and relatively controllable transport of water, ions, and other nutrients through biological channels ensures the success of their essential movements within the organisms [6, 9, 88, 89]. Currently, the process of simulating the biological channels' structure of in cell membranes with the aim of producing artificial membranes, offering high performance and a range of useful functions, has been of enormous technological and scientific interest.

2.2.1.1. Fabrication of membranes with incorporated biological channel proteins

The direct way of producing biomimetic channels is to simulate the structure and composite of the cell membrane. This entails integrating biological channel proteins into the bilayer lipid membranes (BLM), as it is a basic model of the phosphor lipid bilayer for cell membrane [88, 89]. However, the key problem with BLM is the low stability potential. To solve this drawback, the supported BLM on different porous substrates can be implemented [88, 89]. Some of the most popular substrates used include gold, as well as silicon, glass, other metallic thin layers, polymers, and Si₃N₄ [90]. When compared to the organic substrates, the inorganic porous substrates offer a higher number of advantages with regard to the chemical, mechanical,

thermal stability, and lifetime properties [91–94]. Moreover, the block copolymers' self-assembly provides another method for creating a bilayer that can function as an alternative to BLM. This is mostly due to its controllability, greater stability, and the capacity to stop the direct contact of protein to solid substrate, since this can inactivate and immobilize proteins [95]. These biomimetic membranes can be produced using a variety of approaches such as Langmuir-Blodgett/Langmuir-Schaefer monolayer transfer methods, spin-coating, and vesicle rupture. Within these methods, the vesicles rupture approach is one of the easiest to apply and most frequently implement [95]. **Figure 13** outlines the schematic process of producing biomimetic membrane using vesicles rupture method. In the first step, the vesicle incorporated channel proteins are produced using the film rehydration approach (**Figure 13a**). Next, the solution of vesicles is made and then released directly onto the substrates (**Figure 13b** and **c**). Finally, the vesicles proceed to rupture with the aid of covalent interaction or interfacial adsorption, as a result forming the planar bilayer membranes (**Figure 13d**) [92, 94]. To facilitate the suitable interactions with solid substrates, polymers forming the bilayers need to be used in a way that does not alter their self-assembly functionality and structure [92]. The substrates likewise must be functionalized if they are to remain chemically active. Various triblock copolymers end-functionalized with methacrylate, disulfide, and acrylate groups were created so as to react with silanization-modified substrate, gold-coated substrate, and amine using covalent interaction [92]. Gold is frequently selected as the surface modifier for

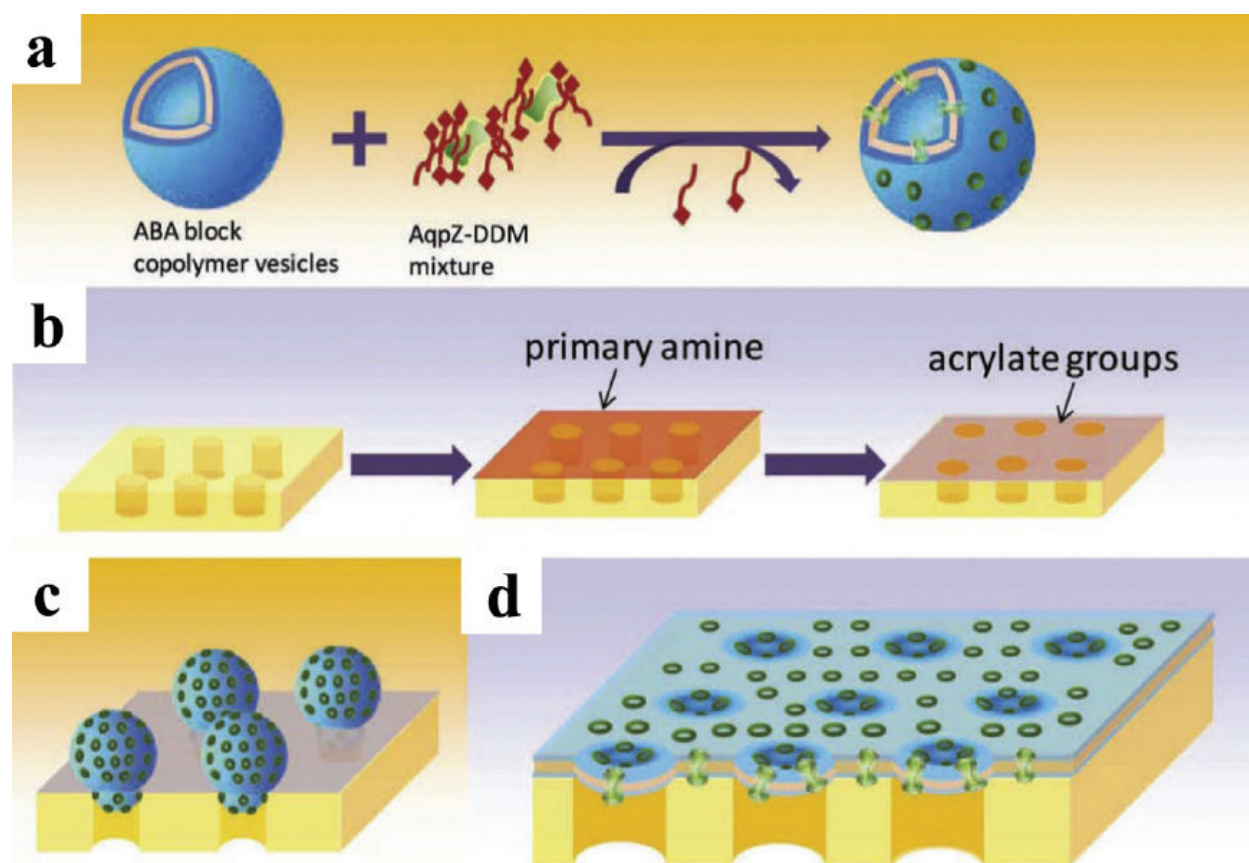


Figure 13. Schematic diagram of pore-spanning membrane design and synthesis. Source: Ref. [94], Copyright 2012; reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

substrates, since it is not cytotoxic, stable, and very active, the latter allowing it to react with polymers and offer new reaction sites for membrane further modifications. **Figure 13b** shows polycarbonate tracked-etched membranes covered with a gold layer so as to attain the subsequent chemisorption of cysteamine monolayer and the later conversion to acrylate. The improved overall stability of biomimetic membranes may be achieved using the process of forming covalent interactions between the acrylate groups on the substrate and the methacrylate groups on triblock copolymer.

Recently, layer-by-layer (LbL) self-assembly and interfacial polymerization were used to develop strong and defect-free AQP-containing membranes that lend themselves to easier scaled up [96, 97]. First, the AQP-containing proteoliposomes were created and then embedded into the membrane's matrix. This helped to create a compatible and stable environment for AQP. These research studies generated valuable new methods for fabrication of biological channel proteins-containing membranes offering improved efficiency. The primary change from the earlier experimental studies is that in this case, AQPs functioned as the dispersed phase within the membrane rather than infiltrate the entire membrane.

2.2.1.2. Membrane fabrication by method of constructing artificial nanopores/nanochannels

Artificially created nanopores/nanochannels featuring functional groups may behave as equivalents of biological channel proteins, due to their great flexibility in terms of shape and size, high stability, chemically and mechanically robust properties, and the various tunable surface qualities [98]. Membranes that possess artificially created nanopores/nanochannels can be produced using bottom-up and top-down routes. What these routes entail is the creation of engineered solid-state nanopores/nanochannels on nonporous substrates using micromachining and then producing nanopores/nanochannels with the aid of self-organization of molecules and atoms, respective of the directions [98]. Specifically, the top-down route is primarily based on electron beam, ion-track-etching, laser, and electrochemical etching technologies, using which the nanopores/nanochannels of varying sizes and shapes on organic and inorganic substrates can be produced [99]. The nanopores/nanochannels developed made with bottom-up route incorporate hexagonally packed cylindrical block copolymer, carbon nanotube (CNT) by chemical vapor deposition (CVD), organic nanotubes by self-assembly, anodic aluminum oxide (AAO) and titania nanotube (TNT) by anodic oxidation, and other using respective methods [100]. If compared with the top-down route, the bottom-up route can help develop membranes with higher pore/channel density potential, a highly beneficial characteristic for molecular separations, as well as other research areas that require a greater channel array area [88, 89]. For example, the AAO porous template may feature a pore/channel density of 10^{15} m^{-2} , while the TNT membrane has a density of $5\text{--}10 \times 10^{13} \text{ m}^{-2}$ pore/channel, a rate that is greater than the natural cells' ion-channel density of nearly 10^{12} m^{-2} [88, 89]. The nanopore/nanochannel entails the channel or pore with a diameter value in the range of 1–100 nm, a number that is bigger than the sizes of most molecules and ions. As a result, the process of entrance or inner surface functionalization is required in order to lower the operational nanopore/nanochannel size or act as the "gate" ion channels located in cell membranes, effectually helping to achieve selective permeation ultimate. Furthermore, for the use of nanoporous membranes in bio-recognition and energy conversion, the process of

inner modification is frequently needed to recognize and immobilize bio-molecules. A common method used for this is the immobilization of functional molecules on the nanopores/nanochannels' interior surface with the help of diversified chemical covalent reactions [101]. For example, gold nanopores/nanochannels can be modified with molecules carrying S-S or SH groups so as to create S-Au bonds, while the oxide surface can be altered using a range of silane derivatives [102]. Alternative approaches to the modification of nanopores/nanochannels are plasma modification, electro-static self-assembly, and the deposition of metals using ion sputtering deposition, electron beam evaporator, or electroless deposition [103]. **Figure 14** outlines an instance of inner surface-modified nanochannel with pH-responsive and employing the chemical covalent type of reaction. In this case, the cylindrical nanochannels with a 15 nm diameter on poly (ethylene terephthalate) (PET) membrane were first produced with ion-tracked technology. Next, the nanochannels were modified with 4,4' azobis (4-cyanopentanoic acid), as a surface-confined polymerization initiator, and a 4-vinyl pyridine as the monomer for forming pH-responsive polymer brushes [98]. These types of brushes can alter their form from the charged hydrophilic state, collapsed, swollen, and neutral hydrophobic state, when an environmental pH alternates between 2 and 10.

Synergistic coassembly of block copolymers (BCPs) and nanotube subunits (cyclic peptide, 8CP) was used to produce thin membranes that include subnanometer organic [104]. First, polymers were tethered onto 8CP so as to augment solubility and help mediate interactions between one part of BCP and 8CP, as shown in **Figure 15**. Once blended with BCPs, the 8CP-polymer conjugates were restricted in the BCP cylindrical microdomains, which have an affinity with polymers, and then formed into nanotubes in the nanoscopic domains once heated by the hydrogen bonding occurring between amino acid residues located on neighboring

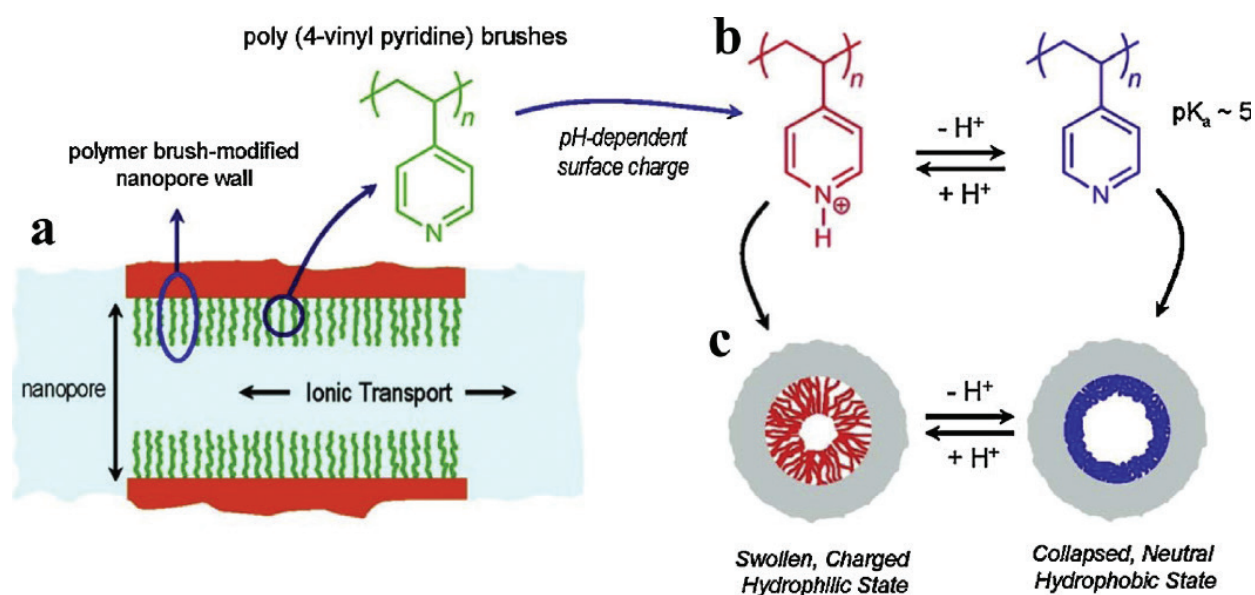


Figure 14. (a) Simplified description of the brush-modified cylindrical nanochannel. (b) pH-dependent pyridine-pyridinium equilibrium occurring in the brush environment. (c) Illustration indicating the conformational changes happening in the brush layer upon variations in the environmental pH. Source: Ref. [98], Copyright 2009; reproduced with permission from the American Chemical Society.

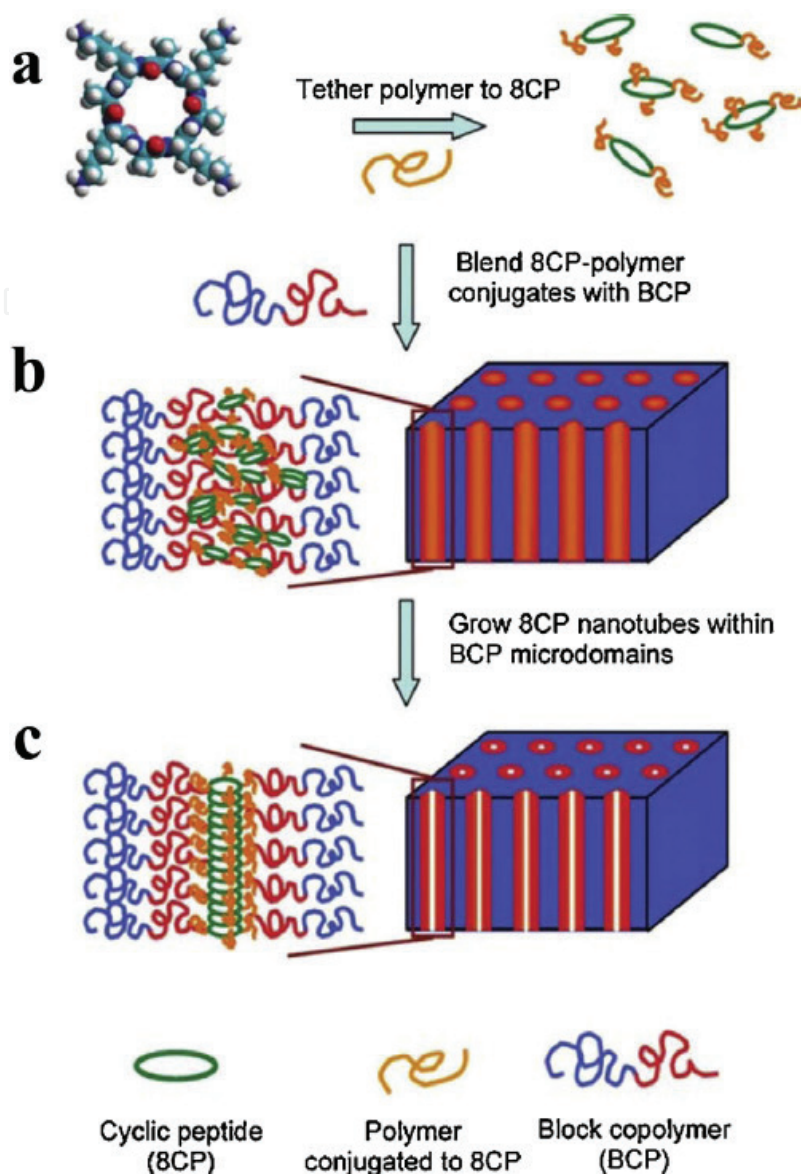


Figure 15. Schematic illustration of the process generating subnanometerporous films using direct coassembly. Source: Ref. [104], Copyright 2011; reproduced with permission from the American Chemical Society.

peptides. Finally, the membranes with sub-nanometer channels, that are oriented in a normal way toward the surface, were successfully created. The shape and size of the nanotubes be tailored through the process of changing the nanotube subunits' molecular structure beyond the restrictions imposed by block copolymer self-assembly. As a result, selective and swift molecular transport can be obtained. Within the artificial nanopore/nanochannel types, the CNT stands out since it functions as an alternative to water channels and biological ion channels due its propensity for narrow diameter, inherent smoothness of the inner surface, and hydrophobicity [105]. Molecular dynamics (MD) simulations have been used to research the transport mechanisms of water and ions in CNT, as well as the possible uses of CNT in membrane processes and applications [106]. Research suggests that water molecules indicate single-file transport in CNT because of the creation of a robust hydrogen bond chain, similar to the

water transport detected in AQP [107]. As a consequence, the CNT's water transport rate is analogous to the one occurring in AQP. To gain higher selectivity values, CNTs are frequently modified at the entrance using organic groups that can help achieve a lower diameter and a more selective ion interaction [108]. While the hands-on applications of CNT-containing membranes, implementing nanochannels in CNT, is rather limited, the possibilities it promises has attracted attention and incited new research directions. Because of its enhanced controllability, high channel density, and superior mechanical robustness, the biomimetic membranes featuring artificial nanopores/nanochannels can be highly relevant to processes that require advanced size-selective separations.

2.2.1.3. Fabrication of membranes via incorporation of artificial nanopores/nanochannels and biological channel proteins

When it comes to this type of biomimetic membranes, the biological channels can guarantee the advantages of intelligence and an atomically precise structure that resembles living cells. Alternatively, the artificial nanopores/nanochannels offer qualities like durability, size, shape control, and robustness. The ion channel protein Gramicidin-A, in the track-etched nanopores with a diameter of 15 nm, was filled on the polycarbonate thin film, while the ion diffusion coefficient of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} ions was measured in order to calculate the nanoporous membrane's selectivity and permeability values [87]. The Gramicidin-A's adsorption into the nanopores was preferred by the surface hydrophilic treatment featuring ethanol and contributed to a greater affinity of Gramicidin-A toward hydrophobic pores rather than toward the hydrophilic surface. It should be noted that although the effective ion diffusion coefficients were amplified after Gramicidin-A inclusion, the increase in values was not as substantial as was expected. This can be due to the fact that the nanopores were not completely filled up with Gramicidin-A, and as a result, the ions likewise diffused within the "free" electrolyte inside the nanopores. Thus, additional experimental research is necessary so as to achieve cases where the entire nanopores are filled out.

2.2.2. Challenges and shortcomings

The overall performance of a biomimetic nanoporous membrane primarily relies on the membrane's channel density, and membrane integrity [91]. Extensive research initiatives have been established with the specific purpose of developing bioinspired and biomimetic membranes that include biological channel proteins. There are still multiple challenges that problematize practical applications of bioinspired and biomimetic membranes: (1) The first challenge is that the membrane channel density is difficult to control [91], determine, and limit, since it needs to make the self-assembly structure unaffected [93]; (2) the second problem is that the channel protein activity needs to be maintained and that limits the preparation process environment [94]; (3) third, it is challenging to make a defect-free bi-layer in large-scale type of production [94]; (4) the fourth challenge is that the costs of production become excessively high because of how complicated the process of extracting proteins can be. Nanoporous membranes featuring artificial nanopores/nanochannels can offer an exiting range of separation applications due to their superior stability; however, they also have to confront a number of common challenges. When it comes to membranes using top-down

routes, the process of the homogeneous modification of interior surfaces through the nanoscale channels, as well as the large-scale modification, is hard to perform successfully on consistent basis. Furthermore, their applications are limited by their lower channel density and the need to use costly equipment. Of all the membranes employing bottom-up routes, the CNT-containing membranes have gained the most attention due to their theoretically superior water permeability. However, the fabrication of large-scale membranes with low selectivity and aligned CNTs is extremely difficult, and this limits their advancement from the theoretical research stages into practical application testing.

2.3. Fabrication of biomimetic and bioinspired membranes based on formations of natural prototypes

2.3.1. Based on biomineralization

Production of bioinspired and biomimetic membranes based on biomineralization is a method that stimulates the creation of inorganic nanoparticles in the polymeric matrix using mineralization reaction that resembles biomineralization that occurs under somewhat milder circumstances. During the last several decades, organic-inorganic hybrid membranes have gained a lot of interest and became widely applicable, since they offer the benefits of stability and rigidity of inorganic moiety, together with the improved adaptability and efficient membrane-forming property in polymeric moiety [109]. At the same time, organic-inorganic hybrid membranes allowed for new properties due to their hybrid structures. The most direct way of producing a hybrid membrane is the process of physical blending of inorganic nanoparticle and polymer. This process is relatively easy to undertake and regulate. One of the drawbacks is the creation of nonselective voids due to collection of inorganic nanoparticles and their lack of proper compatibility with polymeric matrices [110]. The in-situ sol-gel process is an alternative method of producing these types of membranes and may be capable of overcoming this limitation. During the in-situ sol-gel process, the polycondensation and hydrolysis of the inorganic precursors happen under the catalysis of an acid or a base that creates inorganic nanoparticles in a polymeric casting solution [111]. If compared with the physical blending, inorganic nanoparticles can disperse more homogeneously and offer improved compatibility with the polymeric matrix. The sol-gel method likewise has a number of inherent problems, such severe conditions like strong acidic or alkaline environment, and a relatively low controllability [112]. Biomineralization process mixes organic materials with inorganic as it produces materials with hierarchically sophisticated structures and improved physicochemical qualities at normal pressure and temperature values and an almost neutral pH value in an aqueous environment featuring straightforward chemical compositions [15, 113]. These types of materials are much better than many of the artificially synthesized materials because of the critical control that can be exercised over their size, shape, structure, and assembly of constituent parts [15]. The process of biomineralization in nature offers a uniquely rich source of inspiration, when it comes to the design and production of hybrid membranes.

2.3.1.1. Biomimetic mineralization

The process of biomimetic mineralization mimics the biomineralization method during the material-synthesizing using organic inducer to incite the creation of inorganic nanoparticles

from inorganic precursor and as a result producing materials with distinct properties and microstructures [20]. In this case, the inorganic precursor can take the form of metal alkoxide or metal salt. The organic inducer can take the shape of macromolecules, or smaller sized molecules, and have the necessary functional groups and would help activate the inorganic precursor reaction. The macromolecules can be in the form of the amino group for silica and titania or phosphate, sulfate, and carboxylate groups for calcium phosphate and calcium carbonate [114]. For example, the inducers frequently implemented for the creation of silica are macromolecules, such as protein and small molecules comprised of amines and amino acids [115]. The in situ biomimetic mineralization process is an appealing method for the production of hybrid membranes. It prevents the inhomogeneous filler distribution and filler agglomeration that has happened during the physical blending approach, which suffers from harsh conditions like alkaline or strong acidic environment or poor controllability that can occur during in-situ sol-gel method [112]. In order to produce hybrid membranes using the in-situ biomimetic mineralization, two methods have been created. The first method requires the addition of organic inducer and inorganic precursor into the solution that includes membrane-forming polymer. This allows the mineralization process to transpire at the same time as the membrane formation. The second method requires the immersion of the membrane with inducers into precursor-containing solution. For both these approaches, the inorganic precursors interact with organic inducers through metal-organic chelation or electrostatic attraction. As a consequence, the inorganic precursors become enriched in the microdomains near organic inducers, and this in turn creates the necessary conditions and locations for the mineralization reaction to occur and then homogeneously generate inorganic nanoparticles. Recent research has applied both approaches, and varying types of membrane-forming polymers, inorganic precursors, and organic inducers produce diversified hybrid membranes [112].

2.3.1.2. Membrane fabrication using biomimetic mineralization during membrane formation

The process of mixing raw materials is a relatively easy method for producing hybrid membranes using in-situ biomimetic mineralization. In this case, the gelatin-silica hybrid membranes were created by dissolving sodium silicate and gelatin in water, followed by the solidification of the casting solution [112]. As part of this solution, the positively charged amino groups on gelatin molecules absorbed silicic acid oligomers created by sodium silicate through electrostatic attractions that augmented the local oligomer concentration and quickened the polycondensation progression. As a consequence, silica nanoparticles featuring a diameter smaller than 100 nm were created homogeneously in the gelatin matrix. Chitosan (CS) was used as an inducer and was meant to regulate the production of CdS nanoparticles, since it offers superior metal ion adsorption potential [116]. Once the CdCl_2 solution was combined with chitosan, the CS- Cd^{2+} complexes were produced using the adsorption and chelation of the hydroxyl and amino groups on chitosan with Cd^{2+} ions [116]. Once the adsorption and chelation balance were obtained, the fresh sulfocarbamide solution was gradually dropped. After that, the S^{2-} ions were discharged from the sulfocarbamide and then prompted a reaction with the Cd^{2+} ions in CS/ Cd^{2+} complexes so as to generate chitosan/nano-CdS (CS/n-CdS). During this process of membrane production, chitosan or gelatin showcased a minimum of four key roles, that is, creating an especially thin membrane scaffold, inciting in-situ production of

inorganic nanoparticles, restricting the growth of inorganic nanoparticles to the polymeric network, and lowering the particles' accumulation. There are two frequently applied methods for biomimetic mineralization in the case of membrane-forming polymers that do not have mineralization-inducing groups. Specifically, these methods entail adding other organic inducers into the casting solution or grafting functional groups onto the polymers. Although the former approach may appear easier, the organic inducer has to be selected correctly. A problem could occur if the inducer's catalytic activity was too elevated, implying that the inorganic nanoparticles are forming too rapidly, and the nanoparticles will grow and collect in a shorter time period, thus precipitating before the actual membrane casting. Furthermore, the inducers added must be compatible with the membrane-forming polymers within the required range of compositions. During the process of creating silica-containing hybrid membranes, amino group as well as analogous cationic groups can be crucial. In this case, the quaternized modification was applied to poly(vinyl alcohol) (PVA) and poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) [117]. The polymers' quaternary ammonium groups incited the production of silica using a variety of silica sources, while the network created by polymers and silica during the reaction caused the hybrid membranes to be more compact. Moreover, the addition of other organic inducers to the membrane casting solution allowed to form a silica-containing hybrid membrane [118]. While it is a commonly applied membrane-forming polymer, the PVA cannot incite silica formation. Alternatively, gelatin is a popular silification inducer that can be compatible with PVA at low content values. As a consequence, gelatin was selected as the inducer and then added into the PVA solution with the 9/1 (PVA/gelatin) mass ratio. In the next stage, membrane casting solution was created by mixing the PVA-gelatin solution with the precursor silicate solution. Finally, the silica nanoparticles were produced homogeneously within the network of PVA chains.

The process of functionalizing polymers with proper negatively charged groups offers a method for inciting as well as controlling the development of CaCO_3 nanoparticles. For instance, hyperbranched polyglycidol (hb-PG) functionalized using a variety of groups, such as phosphate monoester, sulfate, and carboxylate groups, was implemented during the preparation of CaCO_3 hybrid membranes with the spray technique. The application of this method indicated that the functional group type had a substantial effect on the structure and morphology of CaCO_3 . **Figure 16** shows how phosphate-ester-functionalized hb-PG, sulfate, and carboxylate helped to form calcite composite, vaterite composite, and vaterite-calcite composite, respectively.

Biomimetic mineralization is a water-demanding process because of the implicit need for water during the reactions and water solubility of inducers. As a result, hybrid membranes cannot be developed with the methods mentioned above for water-insoluble polymers, since they require organic solvents in order to dissolve polymers. As a solution for this requirement, the process of water in oil W/O reverse microemulsion was developed. This process is based on the addition of surfactant and the tracing of water inorganic casting solution [119]. In this instance, the water-soluble inducer contacts the oil-soluble inorganic precursor at the interface of two phases and then encourages the hydrolysis-condensation reaction. Once this occurs, the silica nanoparticles are produced in this narrowed space, as outlined in **Figure 17**, and the creation of hydrophobic/oleophilic polymer-silica hybrid membrane is completed.

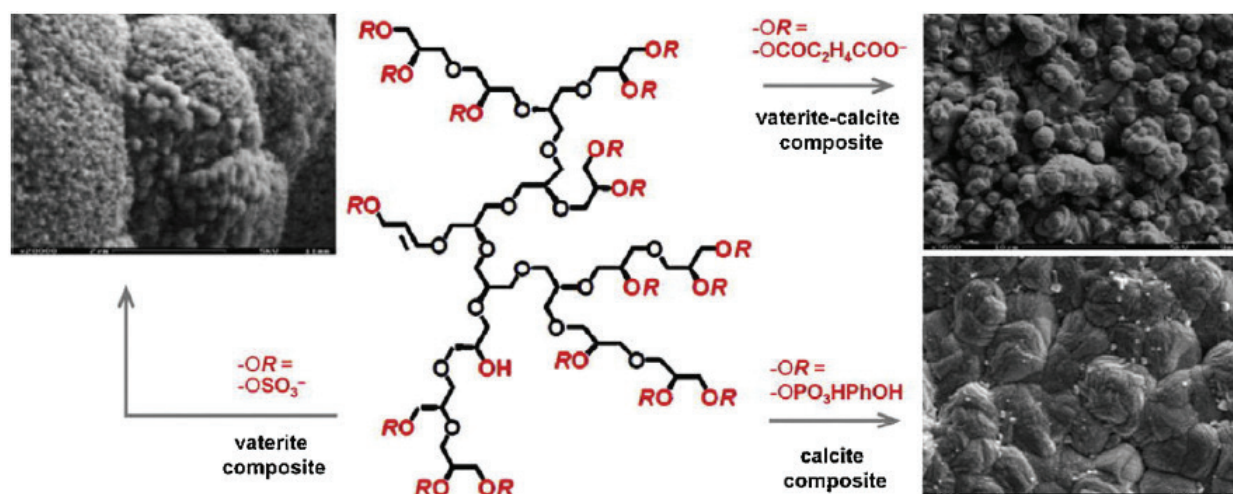


Figure 16. The molecular structure of hb-PG and SEM micrographs of CaCO_3 hybrid membranes formed in the presence of differently functionalized hb-PGs. Source: Ref. [114], Copyright 2012; reproduced with permission from Elsevier Ltd.

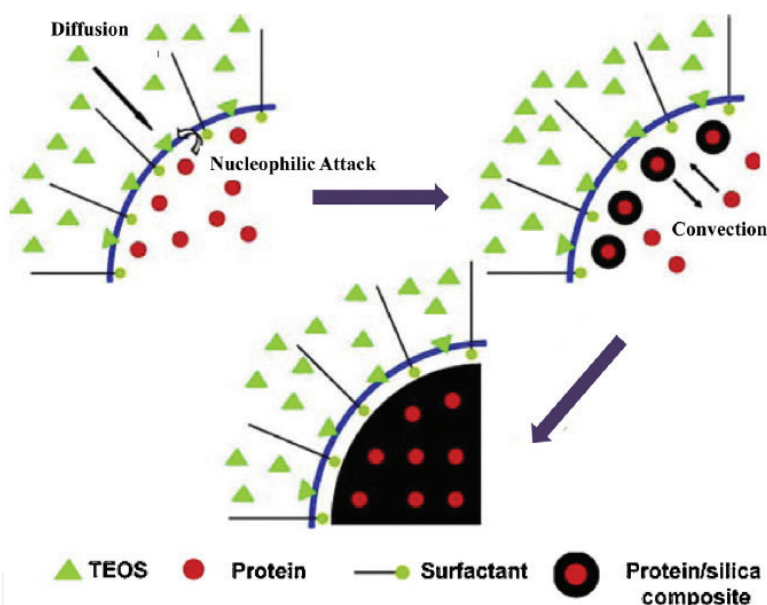


Figure 17. The formation mechanism of silica mediated by macromolecule inducer in reverse microemulsion. Source: Ref. [119], Copyright 2012; reproduced with permission from Elsevier Ltd.

The development of W/O microemulsion was a critical step toward a successful biomimetic mineralization process in hydrophobic/oleophilic polymer solution. In this process, the water in microemulsion has the capacity to dissolve inducers. Water likewise is essential for the hydrolysis reaction of silica precursors, and the water/oil interface guarantees the presence of reaction sites where the mineralization process can occur.

2.3.1.3. Membrane fabrication using biomimetic mineralization after membrane formation

The process of immersing the membrane with inducers into a precursor-containing solution offers a post-treatment method for developing hybrid membranes using the in-situ biomimetic

mineralization. These types of inducers may exist either on the surface or within the membrane's matrix and cause a variety of inorganic nanoparticles' distributions. Recent research suggests that smaller sized molecular inducers, such as amino acids, are seldom applied because of their weaker interactions with membranes and smaller size, since that makes them susceptible to leaking in aqueous solutions [120]. Whenever the inducers are adsorbed solely on the membrane's surface, they can have contact with inorganic precursors once the membrane is immersed into the solution and as a result lead to the creation of inorganic layer on the surface [120]. Microcapsule type membranes were produced with the aid of this approach. In this instance, the sacrificial templates were distributed in protamine aqueous solution for the duration of several minutes, after which they were suspended in titanium-source or silica-source solutions and once the residual protamine was washed away [120]. During this process, the titania or inorganic silica layer was created on the external surface. Whenever the inducers occur within the membrane's matrix and when the membrane-forming polymers have the mineralization-inducing ones, functional groups are mixed and then situated within the membrane, and the inorganic nanoparticles can develop in the membrane's matrix, once it is immersed in the precursor-containing solution [121]. Notably, the process of mineralization happens only if the precursors are diffused into the membrane's matrix and then interact with the inducers, since this ensures that both reaction and diffusion occur simultaneously. The distribution of inorganic nanoparticles is directly connected to the membrane matrix's structure, as well as the rate at which mineralization reaction happens. In most instances, the amount of inorganic components within the membrane slowly lowers as one moves away from the external surface and toward the interior. In a research report, CS membrane was immersed into a simulated body fluid (SBF) for the duration of 3 weeks so as to try and produce hydroxyapatite (HA) [122]. During this experiment, the cationic groups in the CS membrane helped the adsorption of $(\text{PO}_4)^{3-}$ and the subsequent nucleation. The inducer protamine was secured within the confined spaces created by cross-linked PVA molecular chains. During the immersion of the PVA-protamine membrane into the precursor-containing solution, the inorganic precursor first diffused into the membrane's matrix and then generated silica nanoparticles through the templating and catalysis of protamine (**Figure 18**). The silica nanoparticles' sizes could be easily regulated through the controlled alteration of the precursor solution's concentration and pH values. The production of silica nanoparticles may be manipulated by adjusting the membrane matrix structure and altering the annealing temperature so as to control the bulk polymer network and cross-linking of PVA (**Figure 19**). To sum up, biomimetic mineralization method offers an innovative as well as applicable approach for the development of hybrid membranes with homogeneous dispersion, advantageous interfacial interactions under mild conditions, and nanoscale filler sizing. As more research emerges on the mineralization mechanism of biominerals, the process of biomimetic mineralization will gain more ground when it comes to production of diversified hybrid membranes.

2.3.2. Based on bioadhesion

In addition to the separation performance, stability is a key parameter when it comes to the practical aspects of producing a functioning membrane. For those composite type membranes that are made of two distinct layers, the varying surface properties of the two layers

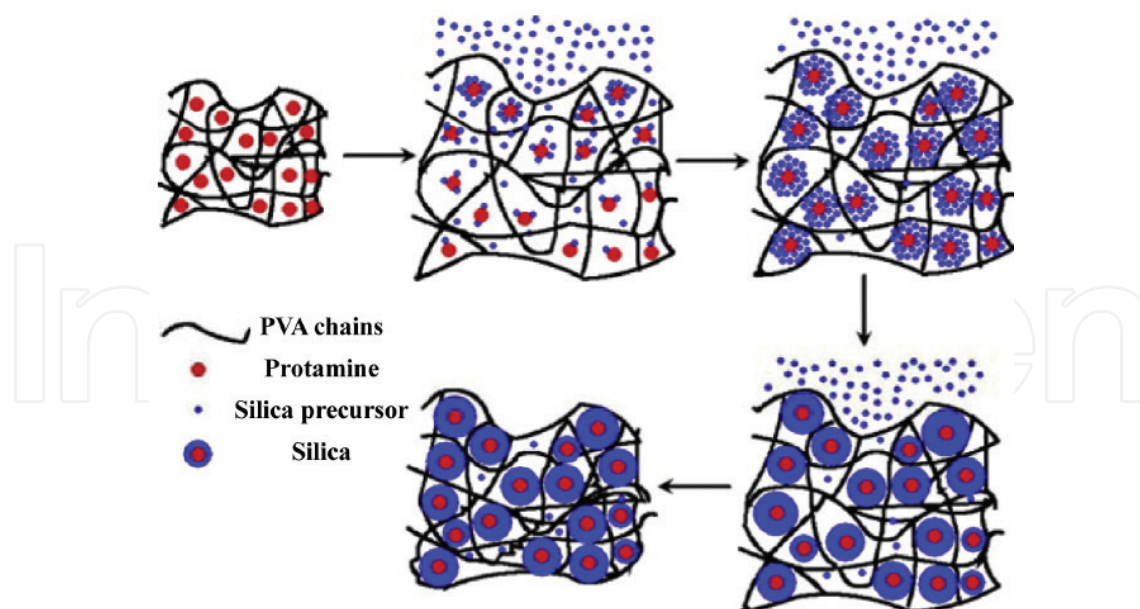


Figure 18. The formation process of silica nanoparticles within PVA matrix. Source: Ref. [122], Copyright 2010; reproduced with permission from Elsevier Ltd.

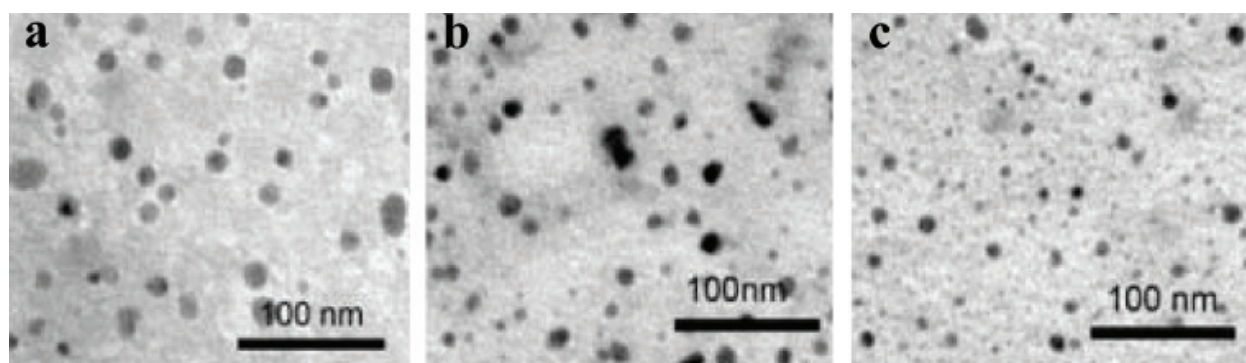


Figure 19. Transmission electron microscopy (TEM) images of silica in the nanohybrid skin layer after it is annealed at (a) 293 K, (b) 333 K, and (c) 373 K. Source: Ref. [122], Copyright 2010; reproduced with permission from Elsevier Ltd.

can cause adverse interface compatibility as well as weakened interfacial interaction between the layers. Whenever the swelling amounts of the two layers are different, a significant stress will appear at the interface. This stress can force the two layers to peel off relatively easily, if the stress surpasses the interfacial interaction. Improving interfacial interaction and interface compatibility between the two layers is an effective and straightforward method for obtaining high stability in composite membranes [123]. When it comes to the surface-functionalized membranes, preserving functional groups during long-time operations is a crucial prerequisite. For membranes with weak interactions between molecular chains and flexible molecular chains, the membrane structure can decline if it is in contact with solvent, water, or other plasticizers during use, since this interaction can significantly decrease selectivity. Enhancing the membrane's cohesive energy will help improve the membrane's stability and maintain its structure. Bioadhesives have served as an inspiration because of

their controllable adhesive/cohesive capacity, greater strength, and broader applicability. In fact, biomimetic adhesion strategies that use bioadhesives, or their analogs like biomimetic adhesives, have been implemented so as to better deal with the challenges listed above.

2.3.2.1. Fabrication of membranes via incorporation of bioadhesives

The addition of bioadhesives as an intermediate layer during the composite membrane production is a relatively easy and efficient way to improve the interfacial interaction between the two layers [124]. Furthermore, bioadhesives that have been derived from natural sources, including dextrin, shellac, and gelatin, are complying with the basic requirement listed as part of the environmental protection. The bioadhesive carbopol (CP) was used for the first time as an intermediate layer for connecting the polyacrylonitrile (PAN) support layer and the CS separation layer. Specifically, CP is a mucoadhesive polymer that features many of the carboxylic groups (COOH) that partially dissociate when in water and offer high viscosity and flexible structure at low concentration values. The schematic depiction of the interface interaction for CS/CP/PAN composite membrane is shown in **Figure 20**. In addition to the carboxy group (COOH) of CP, the hydroxyl group (OH), the amino group (NH₂) of CS, and the van der Waals force, the cyano group (CN) of PAN may generate a multiplicity electrostatic interactions or hydrogen bonds. Once the CP layer is incorporated, the peak peeling strength value was found to be four times greater than that of the CS/PAN membrane. Furthermore, the absolute values of interfacial energy for CP/PAN and CS/CP interfaces were greater than those present in CS/PAN interface based on molecular dynamic MD simulation. The SEM images available in **Figure 21** showcase that the composite membrane features a three-layered structure made up of the support layer,

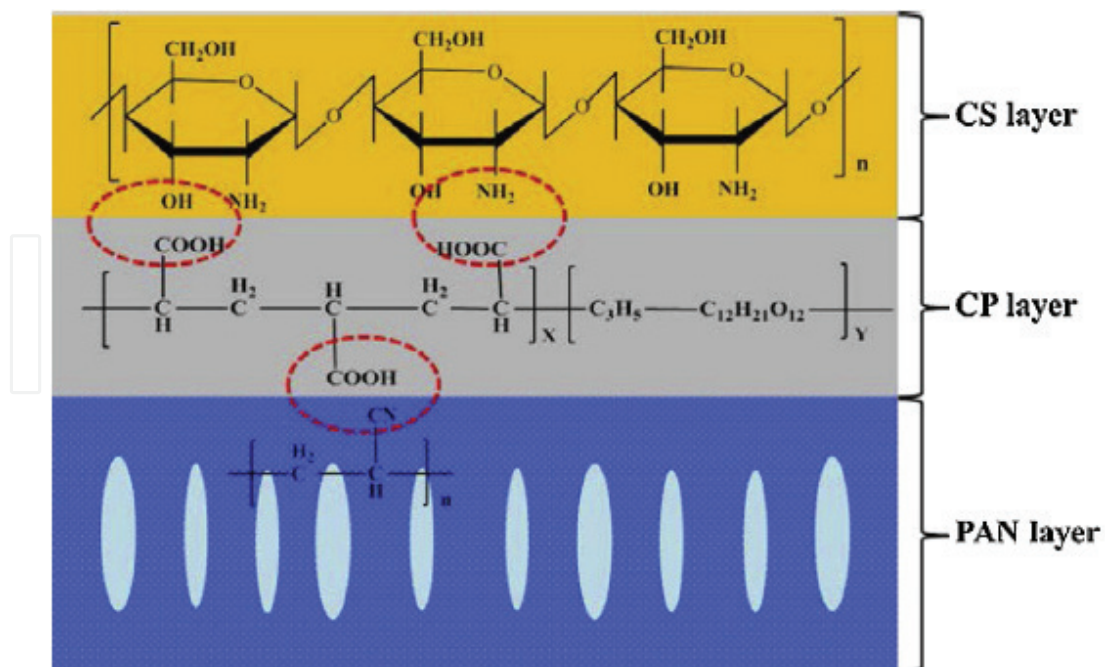


Figure 20. Schematic representation of the interfacial interaction in CS/CP/PAN composite membrane. Source: Ref. [124], Copyright 2010; reproduced with permission from Elsevier Ltd.

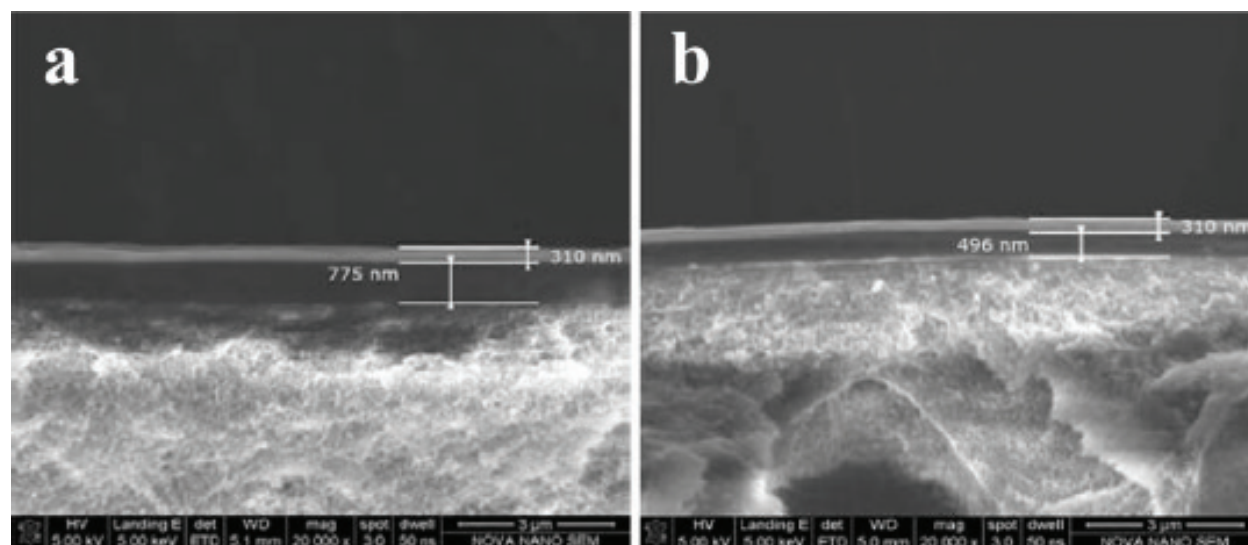


Figure 21. SEM images of cross-section: (a) GCCS(30)/CP(0.5)/PAN membrane, (b) GCCS(30)/CP(0.05)/PAN membrane. Source: Ref. [124], Copyright 2010; reproduced with permission from Elsevier Ltd.

intermediate layer, and separation layer. The fact that there is an intermediate layer has a number of effects on the composite membranes' overall properties and structure. In particular, the additional layer can augment the mass transfer resistance for permeating molecules. The interactions occurring between the intermediate layer and the other layers can affect the stability and structure of interfaces. Moreover, the intermediate layer can function as a defensive coating when it generates a more compatible surface and in turn allows for the casting of polymer solution with low concentration, thus helping to produce a much thinner separation layer.

Cases discussed above focus on bioadhesives that functioned only as the binding agent between the support layer and the separation layer. An argument can be made that if a bioadhesive can generate a thin membrane with selective separation functions, that act as a separation layer while bound tightly to the support layer, then a composite membrane with high structural stability, desirable separation performance, and simple fabrication procedure can be developed [125]. In this case, the bioadhesive that acts as the separation layer needs to possess dual functions of separation and adhesion. These dual functions have varying demands for its chemical and physical properties. The bioadhesive must have a number of specific characteristics so as to provide durable binding to the support layer. These properties can be summed up as follows: (1) numerous polar groups, like OH and COOH; (2) electro negativity; (3) larger molecular weight; (4) flexible chain; and (5) relatively moderate surface tension [126]. Bioadhesive likewise needs to offer advantageous free volume distribution, selective adsorption for one of the permeating molecules, and suitable molecular chain rigidity that can help obtain higher selectivity and permeability. A bioadhesive hyaluronic acid, or a type of acidic polysaccharide, was used for the separation layer of the composite membrane and intended for dehydration of organic solvents because of its excellent chain flexibility, higher molecular weight, elevated negative charge density, favorable membrane-forming properties, and strong affinity to water. MD simulations as well as experimental inquiries were conducted with the aim to corroborate the strong interfacial interaction and promising interface compatibility of this as-prepared composite membrane.

2.3.2.2. Fabrication of membranes via incorporation of biomimetic adhesives

In addition to the bioadhesives obtained from organisms, biomimetic adhesives featuring comparable functional groups and structure can be used as possible alternatives, if the matching bioadhesives are very costly and difficult to extract. As noted earlier, the cement secreted by the sandcastle worm and the adhesive proteins found in mussel byssus contain DOPA that plays an essential role in the bioadhesion process [26]. Dopamine, as an analog of DOPA, has almost identical properties and structural arrangement. Dopamine and DOPA are able to conduct self-polymerization and oxidation under mild conditions in an aqueous environment so as to generate an exceptionally thin coating with favorable biocompatibility, robust interface binding force with diverse substrates, and higher hydrophilicity potential, similar to the operational characteristics of adhesive proteins found in marine organisms [26]. Such an adhesive capacity and enhanced structural stability of the as-prepared coating may be obtained using a range of chemical and physical interactions, for instance, metal chelation, hydrogen-bonding, covalent interaction, and $\pi - \pi$ interaction [34]. Polydopamine (PDA) was added onto various support layers, including PES, PTFE, PSf, and ceramic, before the creation of the separation layer. A number of interactions occurring between the intermediate PDA layer and the other two layers facilitated an enhanced interfacial compatibility between the two contrasting layers, as well as the improved membrane structure's stability for the long-time operation. In a recent experimental setting, PDA layer was used to form a more suitable surface for the interfacial polymerization reaction by actively manipulating the surface roughness, support layer's pore structure, and hydrophilicity. In addition to functioning as the intermediate layer, poly (DOPA)/PDA was likewise used as the membrane's skin layer, like the surface modification coating [127] or the composite membrane's separation layer [34]. If compared to the frequently employed methods, the deposition of poly (DOPA)/PDA is more efficient and green-conscious, as well as advantageous in terms of durability. As illustrated in **Figure 22**, the composite membrane was produced

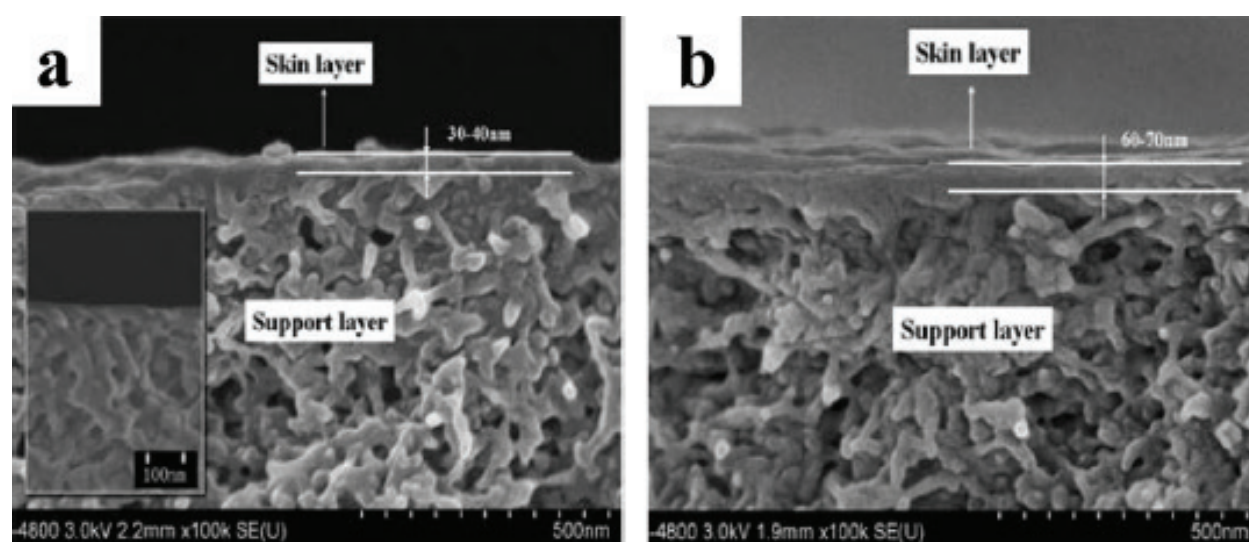


Figure 22. SEM image of the cross-section area of the PDA/PSf composite membranes: (a) single coating (inset: the uncoated PS membrane), (b) double coating. Source: Ref. [34], Copyright 2009; reproduced with permission from the American Chemical Society.

using defect-free and ultrathin PDA separation layer and by immersing the support layer into dopamine aqueous solutions, thus allowing the self-polymerization reaction to happen on the surface [34]. The separation layer's structure and thickness may be controlled through alteration of coating time, number of coats, and the pH and concentration values of dopamine solution. Up until now, the poly (DOPA)/PDA coating has been implemented in membranes that are made out of different materials and feature a variety of pore sizes [127]. In every experimental case, the membrane's hydrophilicity gained visible improvement. However, when it comes to the surface roughness, the values changed depending on the pore sizes found on the membrane's surface. Research also indicated that poly(DOPA)/PDA-coated layer is comprised of accumulated nanoparticles [127]. In the case of MF membrane, pore sizes are bigger than in the case of poly (DOPA)/PDA nanoparticles, which in turn suggests that they are made inside the pores and lead to surface smoothing [128]. In membranes with similar or smaller pore sizes, including reverse osmosis (RO), UF, and nanofiltration (NF) membranes, the process of pore blocking occurs as well as dominates at beginning, thus causing an escalation in roughness [129]. When compared to dopamine, DOPA offers advantageous quality in the form of zwitterionic, as it can help construct a surface with higher hydrophilicity potential.

The poly(DOPA)/PDA derivatives with DOPA/dopamine grafted with other molecules embody an innovative surface modification method that can improve stability, diversity, and operation. The anchoring abilities of mussel adhesive proteins and cell membrane's fouling resistance were integrated through the fabrication of doubly biomimetic copolymer as antifouling coating, which contains both catechol groups and phosphorylcholine (PC) side groups. **Figure 23** showcases that the doubly biomimetic copolymer may be successfully adsorbed onto a range of substrates using the robust anchoring force created by catechol groups,

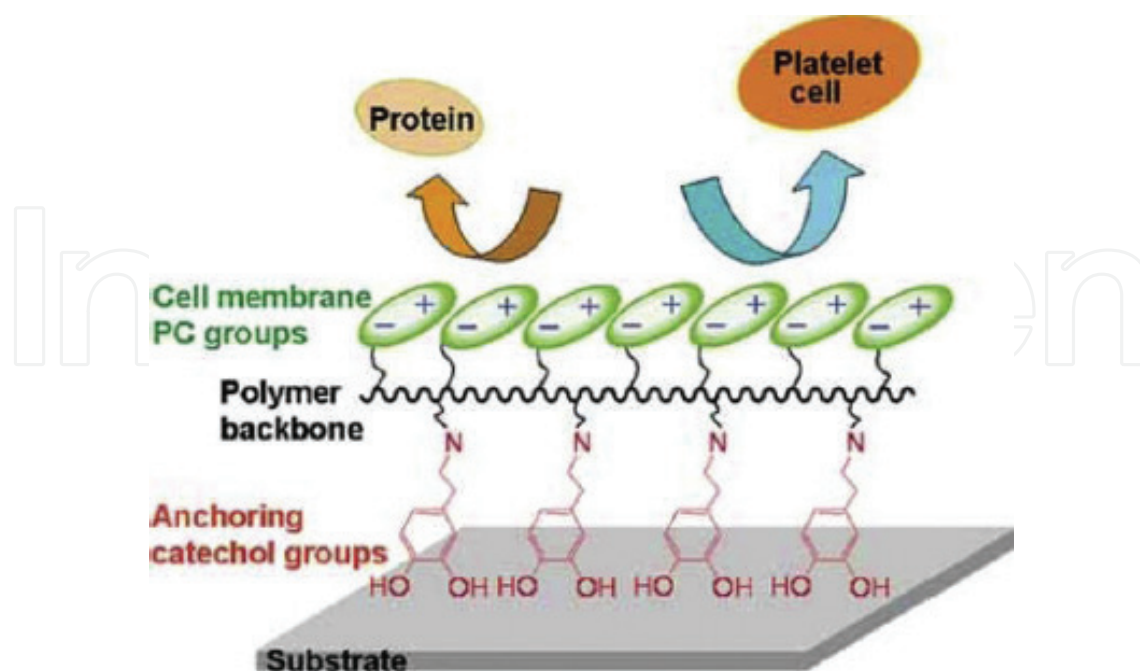


Figure 23. Schematic illustration of the structure and fouling resistance of the doubly coating of biomimetic copolymers. Source: Ref. [130], Copyright 2012; reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

and the PC groups are oriented toward the external side and are creating the antifouling surface resembling cell membrane. As a result, the antifouling surfaces can be generated on different devices and materials with the help of dip-coating in the doubly biomimetic polymer solution. In addition to the enhanced adhesive capacity, Poly(DOPA)/PDA's other advantage is its high reactivity, as it offers reaction sites that help perform additional modifications for the membrane's surface.

Moreover, polyethylene (PE) porous membranes were modified with PDA coating and then immobilized with heparin and bovine serum albumin (BSA), respectively, using covalent bonds in aqueous environment with the aim of gaining improved biocompatibility and higher hydrophilicity. The schematic of the PDA deposition on the PE porous membranes and the subsequent heparin immobilization are shown in **Figure 24**. High numbers of o-benzoquinonyl groups, occurring on the PDA layer's surface after the oxidation and self-polymerization of dopamine, had reacted with the amino/imino groups on heparin, once the membrane was immersed into a heparin solution. As a consequence, the deposition of poly (DOPA)/PDA and their derivatives offers an approach with added versatility and long-time durability that can modify the membrane's surface and help to integrate diverse functions, the latter being particularly valuable for membranes suffering from chemical inertness.

To help increase cohesive energy, as well as membrane's structural stability, dopamine was added into the membrane's matrix as a potential modifier. The polymerization and oxidation of dopamine can happen prior to, during, and after the process of membrane production [132]. A variety of oxidizing agents, such as iron ions, sodium periodate, and oxygen, have been applied in order to encourage the reaction. Multiple interactions between the membrane's matrix and PDA can help make the membrane significantly more stable. Moreover, the adhesive and cohesive balance of PDA, together with the produced membrane structure, may be efficiently regulated through the process of fluctuating the oxidation condition, for example, the ratio of dopamine to oxidizing agent if the production of PDA was during or after membrane's creation, as illustrated in **Figure 25**.

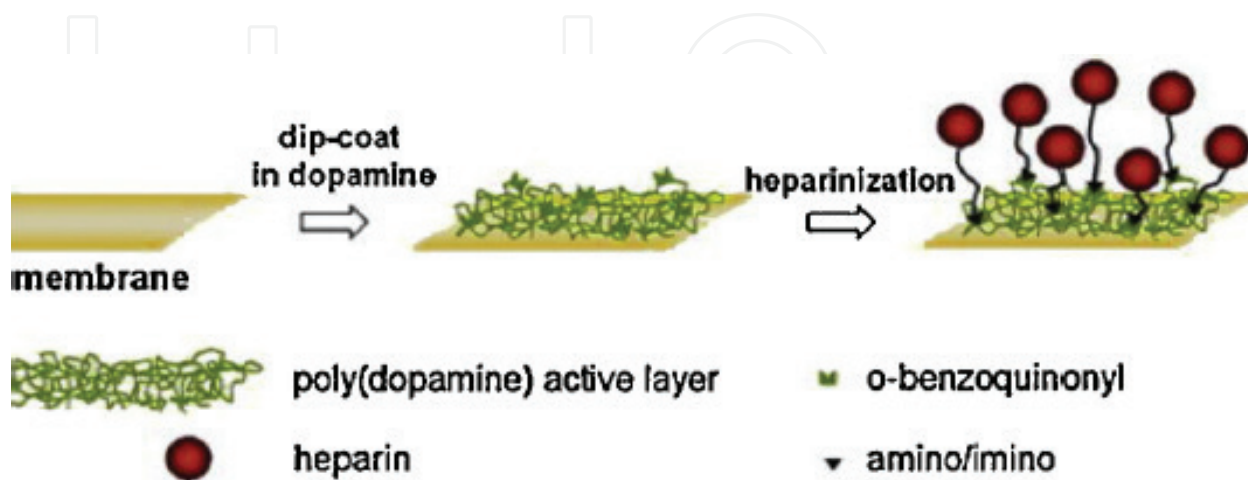


Figure 24. The schematic of the PDA deposition on PE porous membranes and subsequent heparin immobilization. Source: Ref. [131], Copyright 2010; reproduced with permission from Elsevier Ltd.

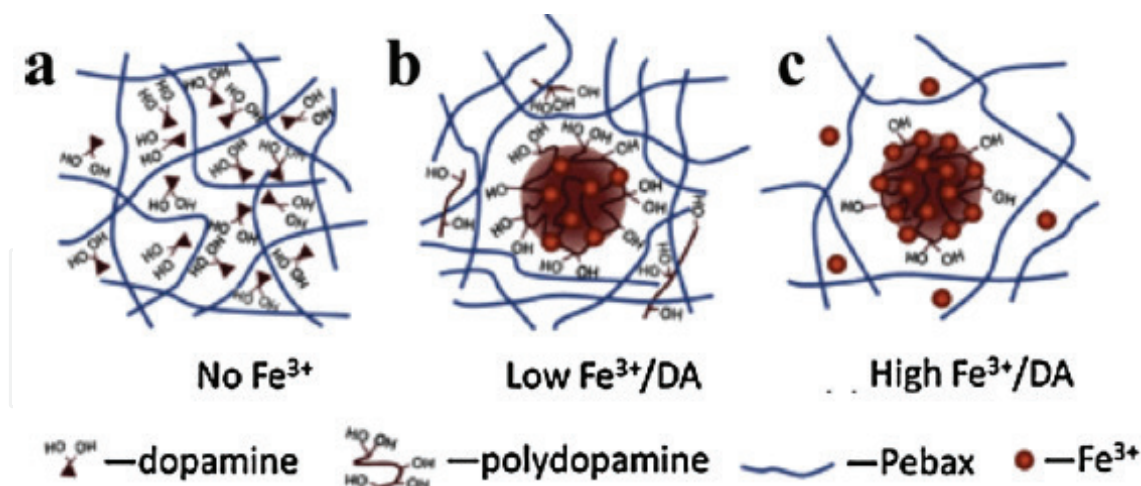


Figure 25. Schematic illustration of the possible nanoscale structures of hybrid membranes with different Fe^{3+}/DA . (a) DA monomers bearing abundant phenyl groups indicate high adhesion ability but weak cohesive ability. (b) Low Fe^{3+}/DA leads to aggregated Fe^{3+} -DA complexes with enhanced cohesive interaction and adequate adhesion ability. (c) High Fe^{3+}/DA leads to robust Fe^{3+} -DA nano aggregates with few available phenyl groups and poor adhesion ability. Source: Ref. [133], Copyright 2012; reproduced with permission from the Royal Society of Chemistry.

2.3.3. Based on self-assembly

Self-assembly can offer an efficient method for duplication of natural manufacturing processes from bioinspired and biomimetic pathways, as both of these share a key characteristic in the form of spontaneous organization, namely biomacropolymer and phospholipids self-assembly. These comparable structures and interaction mechanisms suggest that the self-assembly process offers a distinct nanoscale approach for regulating the membrane's chemistries and structures. The following section provides an outline of various self-assembly processes that are presently used in the production of ordering nanoporous membranes, as well as modification of polymer membranes.

2.3.3.1. Fabrication of membranes via block copolymer self-assembly

The synthetic block copolymers containing two or more thermodynamically conflicting blocks may experience microphase separation into aggregates of multiple morphologies with extremely ordered structures. Microdomain morphologies of diblock copolymers, including cylinders or spheres, are composed of a one phase in a matrix of another, in addition to lamellar and gyroids (**Figure 26**) [134]. Membranes exhibiting improved selectivity and higher flux can be produced using self-assembled block copolymers. Several dense type membranes based on self-assembly of block copolymer were produced with the aim of offering useful applications in pervaporation, fuel cells, and CO_2 membrane separation processes. However, the majority of researchers are turning to the development of nanoporous membranes offering properties such as narrow pore size distributions, tunable chemical and mechanical characteristics, higher porosity, and enhanced ordered and oriented nanopores. For instance, if the composition of block copolymers and the molecular weight happen within specific restrictions, then the spontaneous self-assembly progression can help facilitate ordered cylinders that are aligned perpendicularly with respect to the surfaces and successfully converted into properly ordered nanoporous membranes.

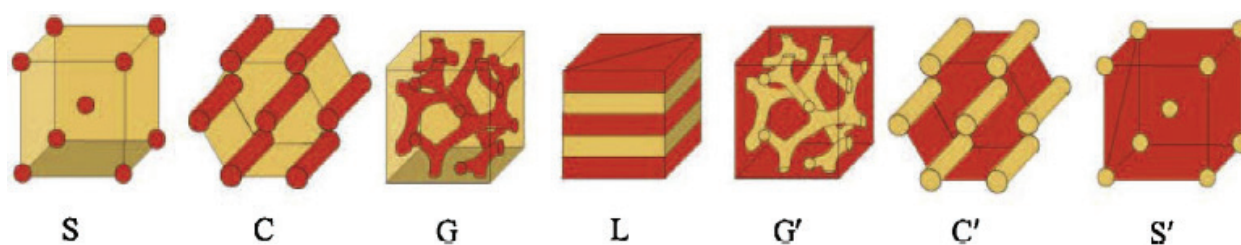


Figure 26. Diagram of the microdomain morphologies of diblock copolymers. Source: Ref. [134], Copyright 2005; reproduced with permission from the Materials Research Society.

Innovative research work has been conducted with the aim of producing nanoporous membranes based on the self-assembly of PS block copolymers with poly (ethylene oxide) (PEO) or hydrophilic poly (methyl methacrylate) (PMMA) blocks. These two approaches were established specifically in order to achieve nanoporous membranes. The first approach relies on the elimination of minor PMMA component that can lead to the creation of cylindrical microdomains oriented in a normal manner with respect to the membrane's surface [135]. The method's representative extremely ordered nanoporous thin films developed using self-assembled PEO-*b*-PMMA-*b*-PS were created through initial solvent annealing that is followed by ultraviolet (UV) irradiation that degrades the PMMA block [136]. The terminal PEO block and the central PMMA block degradability ensure the long-range order within the overall system. Nanoporous type membranes, featuring narrow pore size distribution, have the capacity to provide improved selectivity values as well as enhanced filtration flux potential. The second approach is based on the removal of homopolymer from the block copolymer/homopolymer blends where the homopolymer is more constricted to the cylindrical microdomains' center [136]. Moreover, a double-layered nanoporous membrane was created using a combination of PS-*b*-PMMA together with cylindrical microdomains of homopolymer PMMA. In this case, the film was first constructed on top of the sacrificial silicon oxide layer, after which it was released into the HF solution and then relocated onto the PS membrane's surface. Finally, it was treated by selectively eliminating the PMMA homopolymer from the cylindrical PMMA microdomains using acetic acid (**Figure 27**). As a result of this experimental run, an 80-nm thick membrane was produced with cylindrical 15-nm diameter pores for virus filtration applications.

Poly(lactide) (PLA) is an innovative type of degradable blocks, as well as a multipurpose moiety for developing efficiently ordered nanoporous block copolymer membranes. An approach for making monodisperse nanoporous membranes was designed based on the block polymer PS-*b*-PLA self-assembly [138]. In this instance, a cautious regulation of the copolymer film's solvent evaporation rate can facilitate a perpendicular orientation. Furthermore, the exposure of the composite membrane to a dilute aqueous base can selectively etch the PLA block, thus fabricating a porous structure. The nanoporous membranes were likewise created based on cylinder-forming triblock copolymer polystyrene-*b*-poly (dimethylacrylamide)-*b*-poly(lactide) (PS-*b*-PDMA-*b*-PLA) and PS-*b*-PI-*b*-PLA and the etching of the PLA block. An effective new method was shown to generate strong bicontinuous nanoporous block copolymer self-assembled membranes using the process of ring-opening metathesis polymerization of norbornene-functional PS-*b*-PLA and dicyclopentadiene (DCPD) additive (polymerization induced phase separation), which was then followed by the selective elimination of PLA block [139, 140].

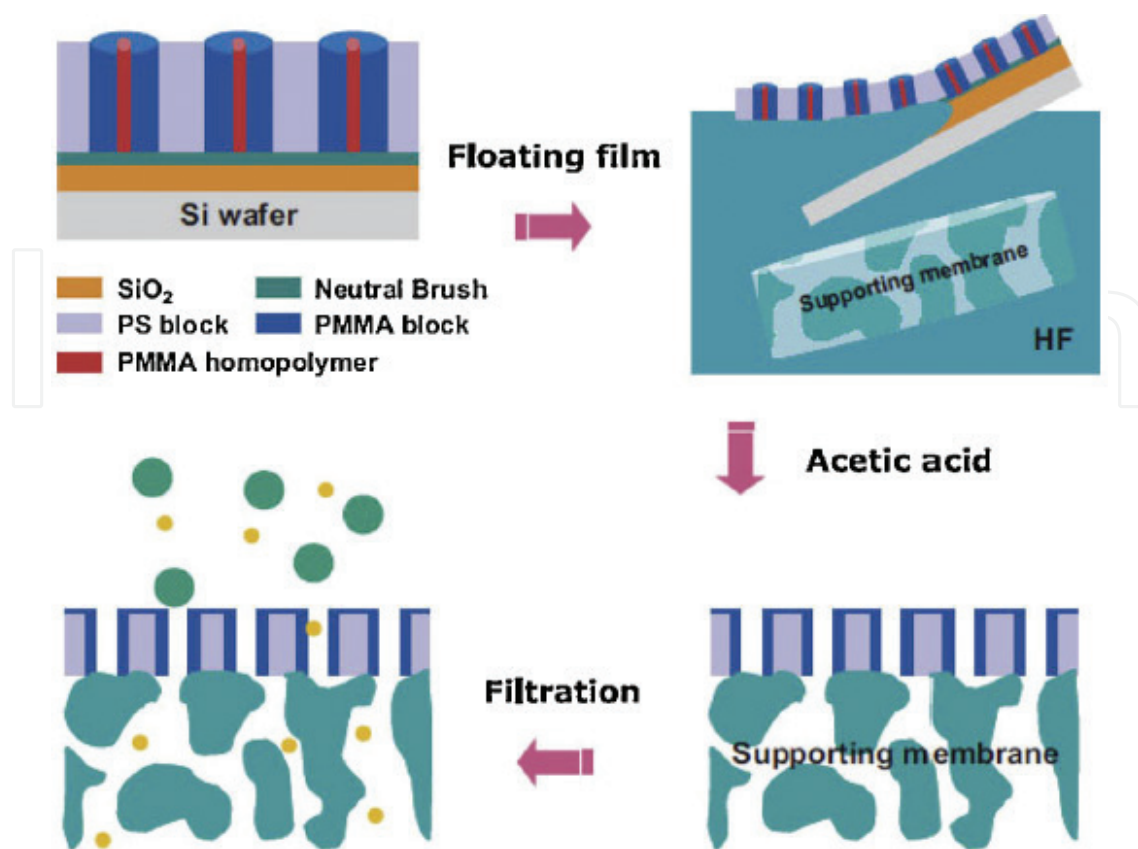


Figure 27. Schematic depiction of the procedure for the production of asymmetric nanoporous membranes through the removal of homopolymer from block copolymer/homopolymer blend films. Source: Ref. [137], Copyright 2006; reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

The application of this method has resulted in the cross-linked nanoporous membranes featuring narrow pore size distributions. Furthermore, PS-based block copolymer composites (PS-*b*-PLA and PS-*b*-PEO) were implemented for the production of ordered nanoporous membranes featuring hydrophilic pore surfaces. The pegylated pore type surfaces were created through the process of degradative elimination of the PLA block from the self-assembled PLA/PEO microdomains. The bicontinuous gyroid morphology together with the hexagonally packed cylindrical morphology was implemented based on the specific annealing circumstances [141]. The PE-based block copolymer composites can likewise be applied during the process of nanoporous membranes' production with hydrophilic pore surfaces and using crystallization-induced self-assembly followed by the PLA removal. Block copolymer composites of PLA-*b*-PE-*b*-PLA and poly(2-(2-methoxyethoxy) ethyl methacrylate)-*b*-polyethylene-poly(2-(2-methoxyethoxy) ethyl methacrylate) (PMe(OE)*x*MA-*b*-PE-*b*-PMe(OE)*x*MA) were responsible for producing a disorderly bicontinuous structure with semicrystalline PE domains and a mixed PLA/PMe(OE)*x*MA domains. An adequately selective PLA etching from the PLA/PMe(OE)*x*MA domains using mild base treatment can effectively manufacture a nanoporous PE with pore walls covered with PMe(OE)*x*MA polymer chains (**Figure 28**) [141].

The uniquely self-assembled block copolymer featuring a cleavable covalent linking unit in the middle of the block copolymer has the capacity to successfully remove small component domains without the application of tough chemicals. An innovative method for producing

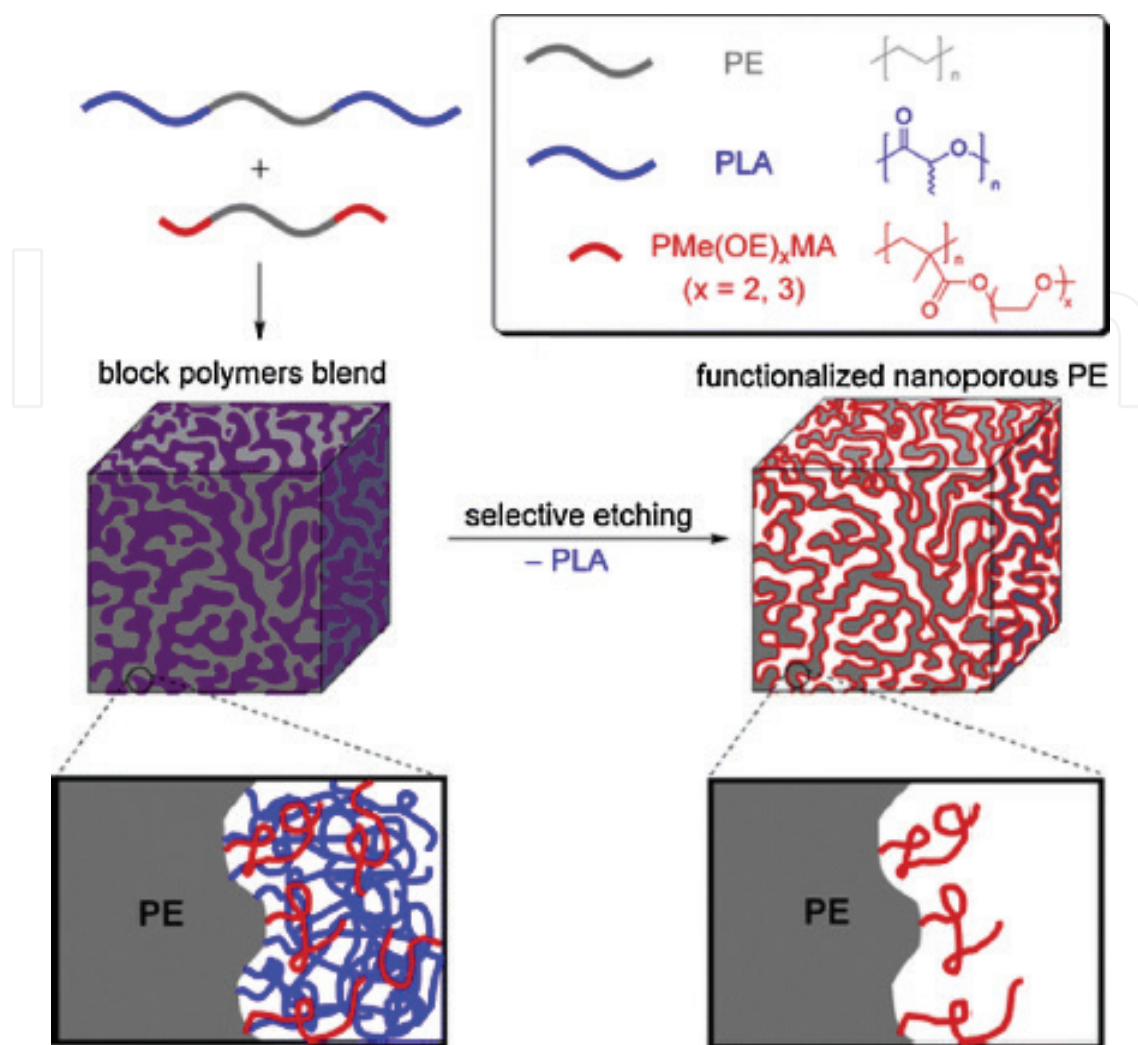


Figure 28. Preparation strategy of the nanoporous PE membrane with pore wall lined with PMe(OE)_xMA by the PLA selective etching from the reactive block copolymer blends. Source: Ref. [142], Copyright 2012; reproduced with permission from the American Chemical Society.

nanoporous PS films was established with the help of a selectively photocleavable PS-*b*-PEO block copolymer (ONB-(PS-*b*-PEO)), where a photochemically sensitive orthonitrobenzyl (ONB) group was fitted in as a type of photocleavable linking unit [143]. In this case, the cylindrical PEO domains can be taken out following the UV light irradiation and the selective solvent rinse. This approach was likewise used to create nanoporous thin films based on PS-*b*-PEO block copolymer carrying a photo-cleavable *o*-nitrobenzyl ester junction. Furthermore, the nanoporous films from the connected poly(styrene-*ss*-ethylene oxide) (PS-*ss*-PEO) were shown through the redox cleavable disulfide bond [144]. Once the annealing in a benzene/water vapor environment had occurred, the PS-*ss*-PEO films had reoriented the PEO cylindrical microdomains in a manner normal with respect to the film's surface. Next, the PEO block could be effortlessly cleaved through the immersion of PS-*ss*-PEO thin films into a *d*, *l*-dithiothreitol-containing ethanol solution, thus forming nanoporous thin films (**Figure 29**). The films accumulated, due to the PS-*b*-PEO acquiring cleavable triphenylmethyl ether junction between PEO and PS, can likewise generate nanopores through the process of selective PEO removal and using trifluoroacetic acid etching [146].

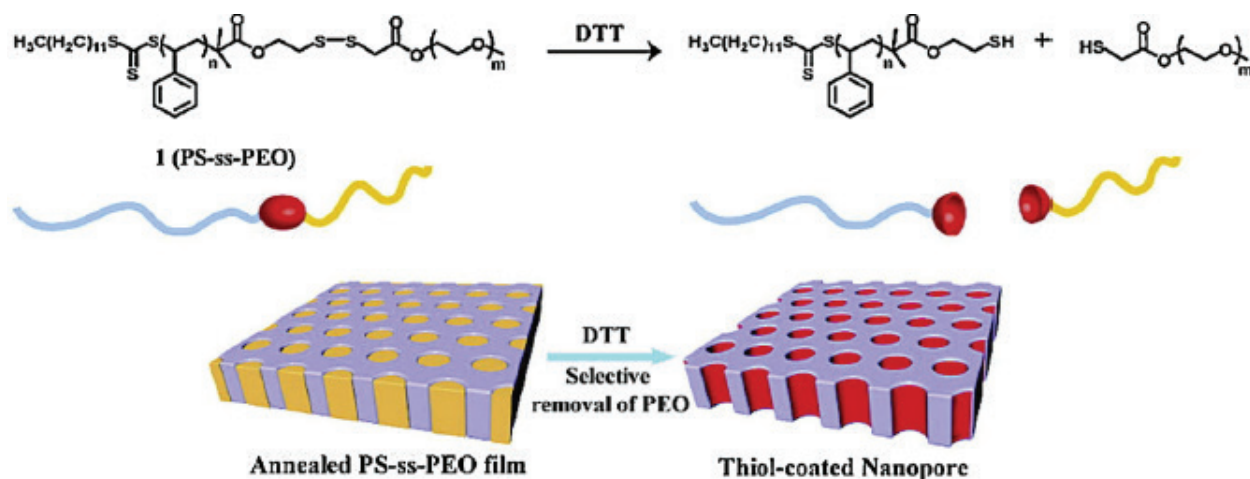


Figure 29. Structure of the PS-ss-PEO block polymer connected by a disulfide bond and schematic representation of the nanoporous thin film preparation. Source: Ref. [145], Copyright 2009; reproduced with permission from the American Chemical Society.

An approach developed with the help of block copolymer supramolecular assemblies together with hydrogen bond donors and acceptors was implemented for the production of ordered nanoporous membranes using the process of removal of minor component enriched nanodomains. Another method relied on hydrogen bonding between 3-pentadecyl phenol (PDP) and 4-vinylpyridine monomer units in order to form a comb-like molecular architecture and effectively alter the gyroid/cylinder morphology of polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP). The two-dimensional films fabricated using such supramolecular assemblies can produce nanoporous membranes through the removal of amphiphilic PDP domains, which occurs when washed with a selective type solvent (**Figure 30**) [147]. Moreover, PS-*b*-P4VP/PDP comb-like block copolymer systems was applied so as to acquire a lamellae-within-cylinders films with periodic and well-defined nanoporous structures. In order to obtain thin films with perpendicularly oriented hexagonally ordered cylinders of P4VP, the 2-(4'-hydroxy benzeneazo) benzoic acid (HABA) was implemented as hydrogen bond donors. Made out of cylindrical nanodomains and generated by P4VP-HABA associates surrounded by PS, the supramolecular assemblies were likewise produced using the PS-*b*-P4VP/HABA system [148]. As part of this process, the HABA molecules made hydrogen bonds with the P4VP units and then uniformly spread within the domain of P4VP (HABA). The HABA could be taken out with relative ease from the P4VP (HABA) domain, once it is rinsed in a selective solvent, which renders a systematic array of nanochannels. Furthermore, substances that can engage with the poly(vinylpyrrolidone) (PVP) block like dodecyl benzene sulfonic acid (DBSA), poly(methyl methacrylate)-dibenzo-18-crown-6-poly(methyl methacrylate) (PMCMA), PMMA, 1,5-dihydroxynaphthalene (DHN), 1-pyrenebutyric acid (PBA), and phenolic resin were similarly applied so as to produce ordered nanoporous films using the self-assembly of block copolymer supramolecules grounded in physical interactions [149].

Figure 31 outlines the two-step method established for the development of the nanoporous structure based on metallo-supramolecular block copolymers with amphiphilic blocks and connected together using metal-ligand complexes. This method's initial stage involves the

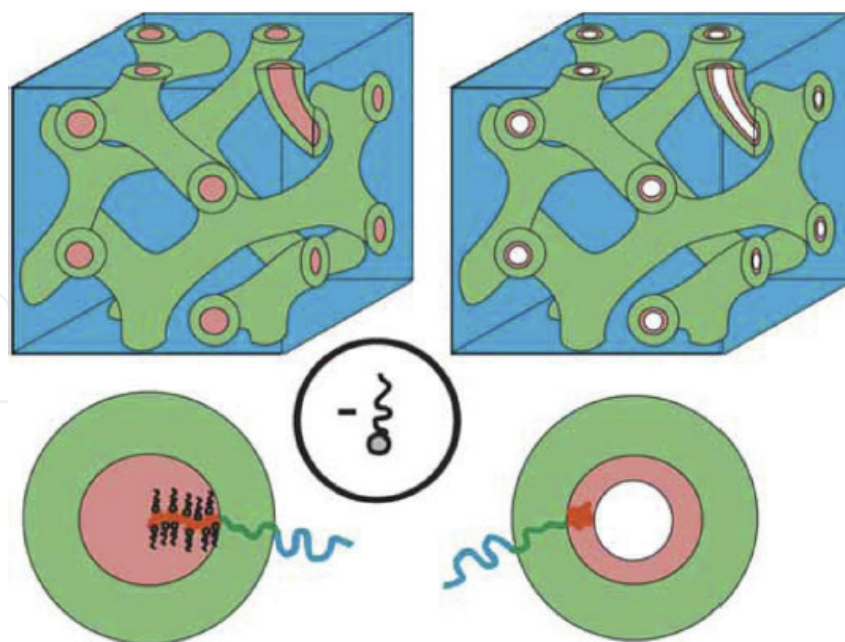


Figure 30. The schematics illustrate supramolecular self-assembly of PS-b-P4VP triblock copolymers. Source: Ref. [147], Copyright 2011; reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

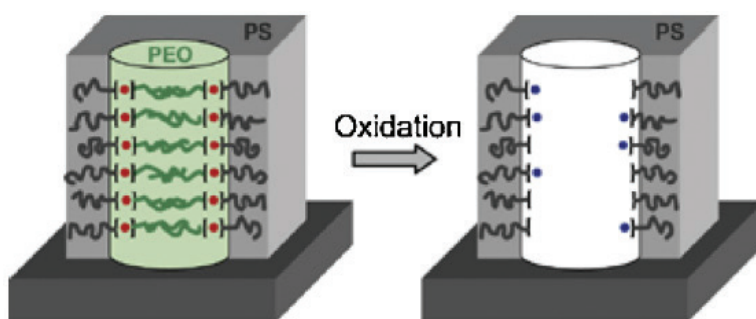


Figure 31. Schematic representation of the preparation of functionalized nanoporous thin films from metallo-supramolecular block copolymers. Source: Ref. [150], Copyright 2005; reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

self-assembly of block copolymer, which then yields cylindrical microdomains oriented in a normal manner with respect to the substrate. The next stage in the process requires opening metal-ligand complex with the aid of redox chemistry that releases minor PEO block and generates nanopores. The metallo-supramolecular block copolymers show superior characteristics in so far as the supramolecular bond's potential reversibility bestows "smart materials" with controllable properties [151].

The overall difficulty of up-scaling, time-consuming preparation steps, and a lack of adequate long-range order are all serious challenges for the process of block copolymer-based membrane development. A new approach was designed for the fabrication of isoporous membranes with nanometer-sized pores based on the idea of joining the self-assembly of block copolymer PS-b-P4VP with the nonsolvent-induced phase separation (NIPS), as shown in

Figure 32 [153]. This solvent evaporation caused a concentration gradient within the block copolymer solution, specifically between the interface turned toward the air section and the interface turned toward the bottom. The microphase separation took place and then moved along the gradient within the greater concentration region of the surface, as a consequence directing the progressive growth of the cylindrical domains into the swollen layer area. As part of the process of phase separation, the nonsolvent water initially moved into the swollen P4VP blocks' cylindrical domains and then was switched with solvent. The solvent coming from the swollen PS matrix was primarily dispersed into the channels, since the interface area available for the solvent/nonsolvent exchange within the channels was significantly greater than the area available at the top surface. Research literature overviews likewise outline innovative methods for producing isoporous asymmetric membranes designer using solvent selectivity, supramolecular assembly of PS-*b*-P4VP block copolymer micelles, and complexation-directed supramolecular chemistry [154]. The supra molecular assembling methods of block copolymer micelles offered a flexible, nondestructive, and relatively low effort way for forming mesoporous block copolymer films featuring well-defined pore size values. The PI-*b*-PS-*b*-P4VP triblock copolymer-derived mesoporous films were produced with a joint application of controlled solvent evaporation, which directed the self-assembly of the terpolymer micelles to structurally shape the mesoporous selective layer, and of NIPS, which shaped the basic macroporous support structure. Once developed, the mesoporous films showed distinctive stimuli responsive permeation behavior.

A confined swelling-induced pore production approach has recently appeared as the latest method for the development of porous materials through the exposure of self-assembled block copolymers to solvents with highly selective minor phase. Some of the synergic benefits of this approach are its higher pore regularity, lack of weight loss, pore forming process reversibility, relative simplicity, and absence of chemical reactions. [152].

A new methodology of collective osmotic shock was formulated with respect to the swelling-induced expansion of the minor phase and the self-assembled block copolymer micelles [155]. At the core of this approach, a spherical block copolymer, or PS-*b*-PMMA, was applied so as to form materials receptive to the influences of collective osmotic shock (**Figure 33a**). In this

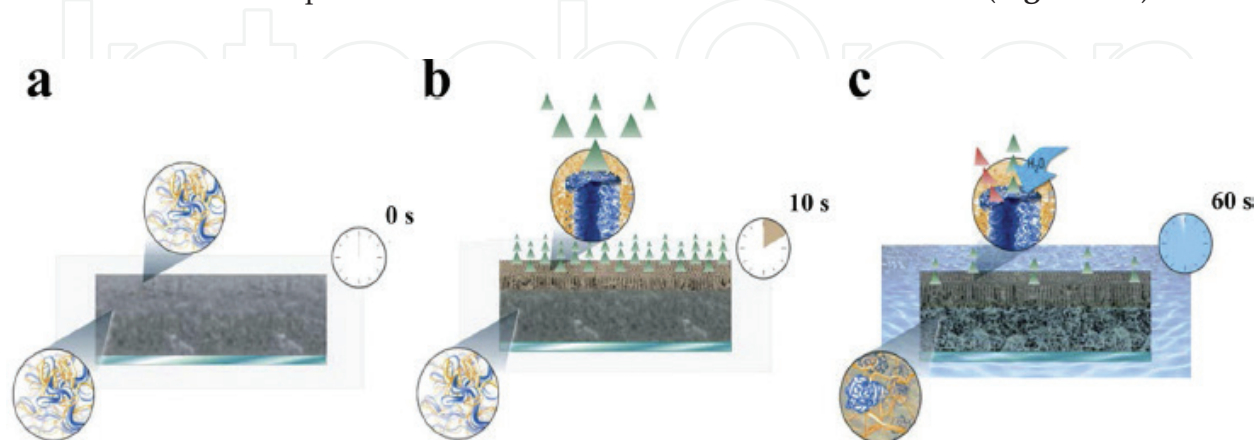


Figure 32. Schematic diagram of the asymmetric film formation process combining NIPS with the self-assembly of block copolymer PS-*b*-P4VP. Source: Ref. [152], Copyright 2007; reproduced with permission from the Nature Publishing Group.

dynamic, the PS-*b*-PMMA film was created using multiple layers of close-packed PMMA spherical cores that were carefully spaced out and enclosed within a PS matrix. The exposure to UV light that followed cross-linked the PS phase and dismantled the PMMA into smaller oligomers. Next, the film was submerged into acetic acid, which is a solvent for PMMA oligomers, and a substantially greater osmotic pressure was created within the PS matrix due to the solvation of degraded PMMA oligomers. This collective osmotic shock caused break-ages among the spheres and formed a path for the complete release of PMMA oligomers. Synchronized and explosive fracture within the structured materials prompted the formation of nanoporated multilayer constructions (**Figure 33b**) that can be applied in ultrafiltration as well as other diversified membrane processes [156].

This section's overview of the ordered porous membranes' production using self-assembly of block copolymers is quickly recapped in **Table 2**. This summary is a convenient reference guide for the production of ordered porous type membranes.

2.3.3.2. Fabrication of membranes via amphiphilic copolymer surface segregation

As an example of an in-situ method for modifying the membrane's surface, the surface separation of amphiphilic copolymers as part of the membrane surface development has shown distinct benefits, including the formation of effective brush layers on pore as well as membrane surfaces [186]. This self-assembly and surface segregation approach may be defined as a series of specific steps. First, the amphiphilic copolymers are mixed into the membrane's casting solution. During the following phase inversion process, the hydrophilic sections of the copolymers close to the interface are separated from the membrane's surface in a spontaneous manner, until the chemical potentials of the brush and bulk layers are balanced. Meanwhile, the hydrophobic sections are securely trapped within the membrane's matrix with the help of hydrophobic interaction [187]. Until recently, the majority of porous membranes were created using surface segregation of amphiphilic copolymers together with the commercially applied membrane production method called the wet phase inversion. In particular, PEO-based comb polymer and methyl methacrylate (MMA) were applied as the surface-segregating additives that would enhance PVDF (polyvinylidene fluoride) membrane's surface hydrophilicity potential.

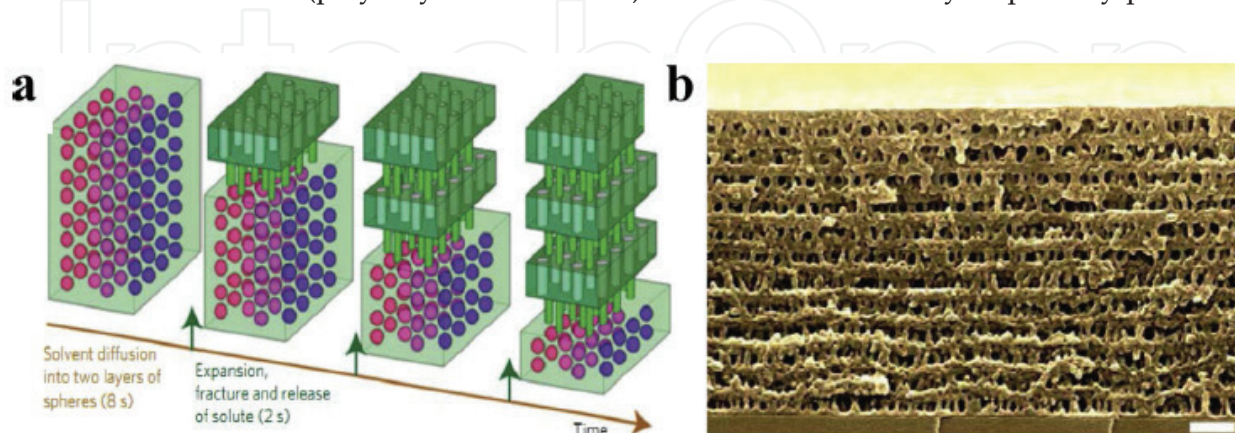


Figure 33. (a) Schematic of the osmotic shock process acting on layers of spheres and leading to the perforated multi layers. (b) Fracture cross-section of PS-*b*-PMMA multilayer structures (scale bar, 200 nm). Source: Ref. [155], Copyright 2012; reproduced with permission from the Nature Publishing Group.

Membranes	Assemblies and assembly approaches	Pore generation	References
PS-b-PI	PS-b-PI; coating PS-b-PI onto silicon substrates, followed by solvent evaporation	Degrading PI by O ₃ and methanol rinsing	[157]
PS	PS-b-PMMA; coating PS-b-PMMA onto PS-r-PMMA neutral layer, followed by vacuum high temperature annealing and rapid quenching	Degrading PMMA by UV exposure and acetic acid rinsing	[137, 158, 159]
PS	PEO-b-PMMA-b-PS; coating PEO-b-PMMA-b-PS onto silicon substrates, followed by solvent annealing; PEO block-permitting long-range ordering	Degrading PMMA by UV exposure and acetic acid rinsing	[136, 160]
PS	(PS-r-BCB)-b-PMMA; coating (PS-r-BCB)-b-PMMA onto P(S-r-BCB-r-MMA) neutral layer, followed by thermal annealing and cross-linking at elevated temperatures	Degrading PMMA by UV exposure and acetic acid rinsing	[161]
PS	PS-b-PMMA; coating PS-b-PMMA onto glass substrates along with fast solvent evaporation	Degrading PMMA by UV exposure and acetic acid rinsing	[135, 162]
PS	PS-b-PMMA/PEO; coating PS-b-PMMA/PEO onto silicon substrates, followed by solvent annealing	Removing PMMA/PEO domains by UV exposure and acetic acid rinsing	[163]
PS-b-PEO	PS-b-PEO/PAA; coating PS-b-PEO/PAA onto porous supports along with fast solvent evaporation	Removing PAA by soaking in water	[164]
PS-b-PMMA	PS-b-PMMA/PMMA; coating PS-b-PMMA/PMMA onto PS-r-PMMA neutral layer, followed by vacuum high-temperature annealing and rapid quenching	Degrading PMMA by acetic acid rinsing	[165, 166]
PS	PS-b-PLA; coating PS-b-PLA porous support, followed by controlled solvent evaporation	Removing PLA by dilute aqueous base rinsing	[138]
PS-b-PI	PS-b-PI-b-PLA; coating PS-b-PI-b-PLA onto hexamethyldisilazane neutral layer or porous supports, followed by vacuum high-temperature annealing	Removing PLA by dilute aqueous base rinsing	[167]
PS-b-PDMA	PS-b-PDMA-b-PLA; molding PS-b-PDMA-b-PLA, followed by vacuum high-temperature annealing	Removing PLA by dilute aqueous base rinsing	[168]
PS	NPS-b-PLA/DCPD; cross-linking NPS-b-PLA/DCPD using the Grubbs catalyst, followed by controlled solvent evaporation	Removing PLA by dilute aqueous base rinsing	[139, 140]
PS/PS-b-PEO	PS-b-PEO/PS-b-PLA; controlled solvent evaporation followed by vacuum high-temperature annealing	Removing PLA by dilute base or concentrated HI solution rinsing	[141, 169]
PE	PLA-b-PE-b-PLA; melt molding, followed by cooling induced PE crystallization	Removing PLA by dilute aqueous base rinsing	[170]
PE/PMe(OE) _x MA-b-PE-b-PMe(OE) _x MA	PMe(OE) _x MA-b-PE-b-PMe(OE) _x MA/PLA-b-PE-b-PLA; melt molding, followed by cooling induced PE crystallization	Removing PLA by dilute aqueous base rinsing	[142]

Membranes	Assemblies and assembly approaches	Pore generation	References
PE	PS-b-PE; melt molding, followed by cooling induced PE crystallization	Removing PS by fuming nitric acid	[171]
PB	PB-b-PDMS; coating PB-b-PDMS onto glass substrates along with controlled solvent evaporation	Removing PDMS by tetra-n-butylammonium fluoride solution	[172]
PS	(ONB-(PS-b-PEO)); coating (ONB-(PS-b-PEO)) onto silicon substrates, followed by solvent annealing	Removing PEO by UV cleavage of ONB and methanol rinsing	[143]
PS	PS-ss-PEO with disulfide juncture; coating PS-ss-PEO onto silicon substrates, followed by solvent annealing	Removing PEO by DDT cleavage of disulfide juncture and ethanol rinsing	[145]
PS	PS-b-PEO with triphenylmethyl ether juncture; coating PS-b-PEO onto silicon substrates, followed by solvent annealing	Removing PEO by trifluoroacetic acid cleavage of triphenylmethyl ether juncture and methanol rinsing	[146]
PS	PS-b-PEO with o-nitrobenzyl juncture; coating PS-b-PEO onto silicon substrates, followed by solvent annealing	Removing PEO by UV cleavage of o-nitrobenzyl ester and methanol rinsing	[144]
PtBOS-b-PS-b-P4VP	PtBOS-b-PS-b-P4VP/PDP; coating PtBOS-b-PS-b-P4VP/PDP onto glass substrates, followed by solvent annealing	Removing PDP by ethanol rinsing	[147]
PS-b-P4VP	PS-b-P4VP/PDP; molding along with vacuum high-temperature annealing and rapid quenching	Removing PDP by ethanol rinsing	[148]
PS-b-P4VP	PS-b-P4VP/HABA; coating PS-b-P4VP/HABA onto silicon substrates, followed by solvent annealing	Removing HABA by methanol rinsing	[173]
PS-b-P4VP	PS-b-P4VP/HABA; casting PS-b-P4VP/HABA on porous support followed by nonsolvent induced phase inversion	Removing HABA by ethanol rinsing	[86]
PS-b-P4VP	PS-b-P4VP/PBA; coating PS-b-P4VP/PBA onto silicon substrates, followed by solvent annealing	Removing PBA by ethanol rinsing	[174]
PS-b-P4VP/DBSA	PS-b-P4VP/DBSA/PDP; coating PS-b-P4VP/DBSA/PDP PBA onto silicon substrates, followed by controlled solvent evaporation	P4VP/DBSA domains collapsing upon annealing	[149]
PS-b-P4VP/PMCMA	PS-b-P4VP/PMCMA; coating PS-b-P4VP/PMCMA onto silicon substrates, followed by controlled solvent evaporation	P4VP/PMCMA domains collapsing upon annealing	[175]
PS-b-P4VP	PS-b-P4VP/DHN; coating PS-b-P4VP/DHN onto silicon substrates, followed by controlled solvent evaporation	Removing DHN by methanol rinsing	[176]
Phenolic resin	PS-b-P4VP/phenolic resin; coating PS-b-P4VP/phenolic resin onto silicon substrates, followed by controlled solvent evaporation	Removing PS-b-P4VP by pyrolysis	[177]
PS	PS-[Ru ²⁺]-PEO; coating PS-[Ru ²⁺]-PEO onto silicon substrates, followed by solvent annealing	Removing PEO by oxidizing the Ru(II) into Ru(III)	[150, 178]

Membranes	Assemblies and assembly approaches	Pore generation	References
PS	PS-[Ni ²⁺]-PEO; coating PS-[Ni ²⁺]-PEO onto silicon substrates, followed by solvent annealing	Removing PEO by methanol rinsing	[179]
PS-b-P4VP	PS-b-P4VP; casting PS-b-P4VP onto glass substrates, followed by initial solvent evaporation and nonsolvent-induced phase inversion	Solvent/nonsolvent exchange	[153]
PS-b-PEO	PS-b-PEO; casting PS-b-PEO onto glass substrates, followed by initial solvent evaporation and nonsolvent-induced phase inversion	Solvent/nonsolvent exchange	[180]
PI-b-PS-b-P4VP	PS-b-PS-b-P4VP; casting PS-b-PS-b-P4VP onto glass substrates, followed by initial solvent evaporation and nonsolvent-induced phase inversion	Solvent/nonsolvent exchange	[181–183]
PS-b-P2VP	PS-b-P2VP; coating PS-b-P2VP onto silicon substrates, followed by controlled solvent evaporation	Shrinkage of P2VP chains after ethanol swelling	[184, 185]
PS	PS-b-PMMA; coating PS-b-PMMA onto silicon substrates, followed by high-temperature annealing	Degrading PMMA by UV exposure and acetic acid initiated collective osmotic shock	[155]

Table 2. Membrane fabrication using the block copolymer self-assembly.

The PEO side chains can connect to the membrane's surfaces because of their affinity to water. PEO side chains likewise display a long-lasting surface hydrophilicity property. PEO brushes, taken away from the surface during cleaning or operation, may be largely restored through additional segregation of the residual amphiphilic additives during the subsequent heat treatment or when others are driven by the developing gradient in the additives' chemical potential. In order to create porous membranes that follow the phase inversion method, amphiphilic copolymers were likewise applied as additives and include hyper-branched star polymers, comb-like copolymers, and block copolymers. Blended membranes had undergone testing in water at 60°C so as to assess the retentive stability of various amphiphilic polymers on the membrane's surface [188]. The testing showed a minor variation in water contact angles in blend membranes when they were continuously leached in hot water for the duration of 30 days, thus reflecting advanced membrane surface strength. Furthermore, a Pluronic block copolymer, poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (PEO-b-PPO-b-PEO), was applied as a surface-segregating additive for the creation of improved fouling resistant PES type membranes. The hydrophobic PPO segments in Pluronic block copolymers became securely fastened in the PES matrix and resulted in the covering of Pluronic block copolymers on PES. Alternatively, the hydrophilic PEO segments slowly drifted to the membrane's surface and lead to a membrane surface featuring improved stability and enhanced hydrophilicity (**Figure 34**) [190]. Moreover, high-performance PES/Pluronic membranes that show stable hydrophilic character and elevated flux values were developed using vapor-induced phase separation combined together with the nonsolvent-induced phase separation approach.

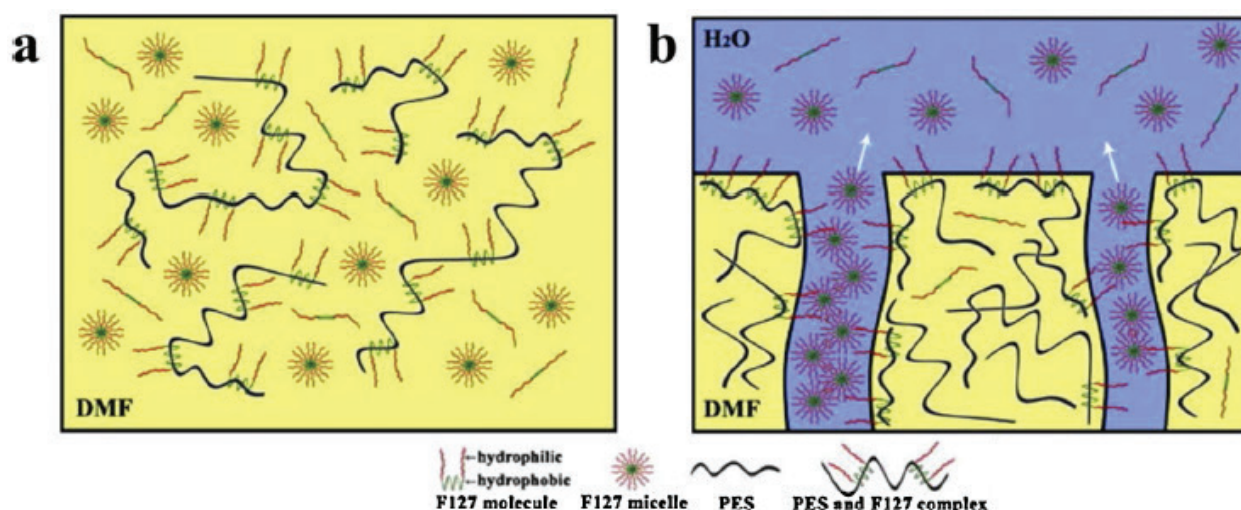


Figure 34. Illustration of dual roles of Pluronic F127 in the membrane formation process. (a) The self-assembly polymers lead to three forms of Pluronic F127 existing in a homogeneous casting solution. (b) Immersing the film in a water bath leads to phase separation and formation of ordered structure and pores within the membrane. Source: Ref. [189], Copyright 2008; reproduced with permission from Elsevier Ltd.

The design strategies for zwitterionic membrane surfaces were developed with the help of alternative amphiphilic zwitterionic ligands used as surface-segregating additives and included sulfobetaine copolymer, phosphorylcholine copolymer, and soybean phosphatidyl-choline [191]. As part of the phase-inversion procedure during membrane production, the surface segregation of zwitterionic segments was conducted spontaneously. This generated zwitterionic brushes on the membrane as well as pore's surface and lowered interfacial free energy value. Moreover, a forced surface segregation approach was applied to in-situ engineering process of a porous amphiphilic membrane's surface, with hydrophilic fouling resilient domains and lower surface free energy fouling release self-cleaning domains [192]. Lower surface energy segments, like silicone-segments or fluorine-containing segments, are not capable of spontaneous separation from the polymer-water interface, due to the unfavorable thermodynamics during NIPS process conducted through the free surface segregation [193]. As part of the NIPS procedure, hydrophilic segments were anticipated to separate at the membrane's surface coordinated by the amphiphilic copolymers' self-assembly. Alternatively, the covalently binding nonpolar hydrophobic sections were pulled onto the membrane's surfaces by hydrophilic segments using forced surface segregation (**Figure 35**). Due to the innate self-healing capacity of surface segregation methods, the long-term surface stability of the low surface energy sections located on the membrane surfaces was likewise anticipated.

2.3.4. Challenges and shortcomings

The prototypes inspired by nature considerably enhance the range of artificial material syntheses and their applications. The process of first extracting central principles at the core of natural material production and then imitating these processes is a rewarding method for replicating comparable physical and chemical structures. However, the complexity and

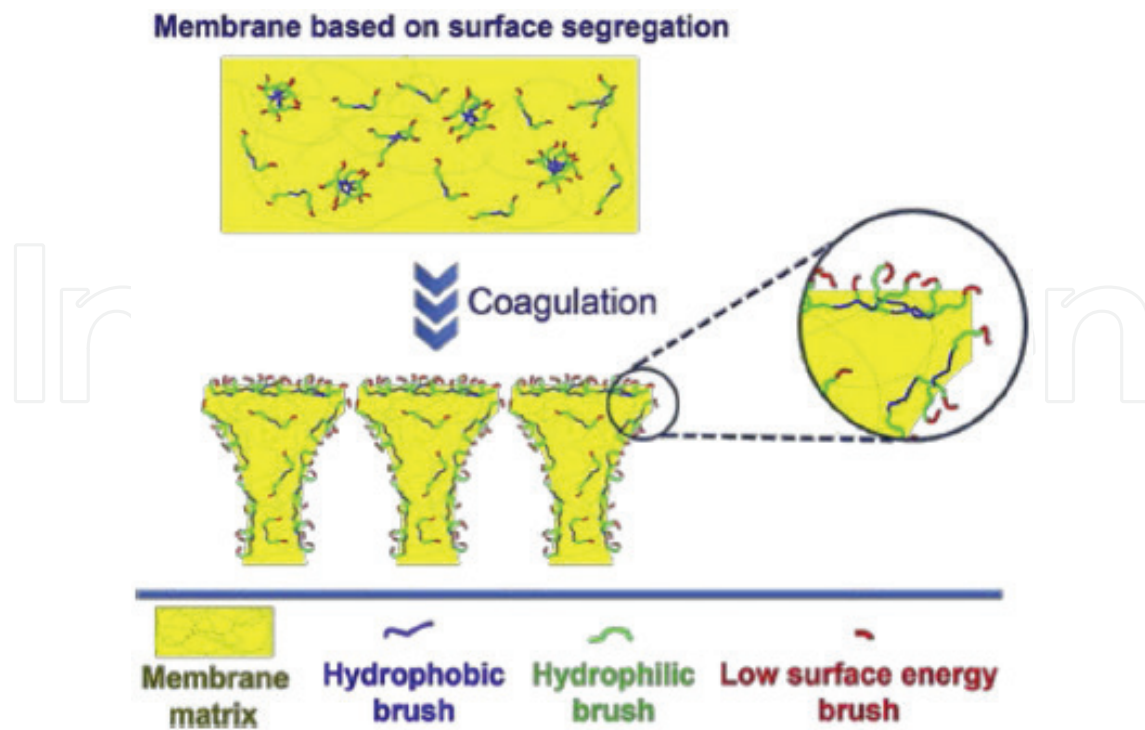


Figure 35. Forced surface segregation process during the membrane formation process.

precision involved in the formation of materials is difficult to imitate or grasp in its entirety. Some of the shortcomings and challenges faced by membrane-fabrication approaches based on simulations of natural prototypes are provided in **Table 3**.

2.4. Fabrication of bioinspired and biomimetic membranes based on functions of natural prototypes

2.4.1. Based on self-cleaning

The classification of self-cleaning surfaces is divided into hydrophobic and hydrophilic, as underwater oleophobic, type of surfaces. When it comes to the hydrophobic or oleophobic self-cleaning type surfaces, the interactions between the hydrophobic epicuticular waxes and multiscale geometrical surface structures are directly inspired by the surface characteristics of lotus leaves or other epidermis and plant leaves with similar properties. In fact, this correlation to the lotus leaves ensures that the hydrophobic self-cleaning type surfaces have an elevated water contact angle or a smaller sliding angle, which indicates low adhesion and superior hydrophobic or functionality. Alternatively, for the underwater oleophobic or hydrophilic self-cleaning surfaces, the correlation of elevated hydration energy moieties and physical heterogeneity, incited by the hydrated skin surfaces in marine organisms, suggests a greater underwater oil contact angle that helps to avert oil fouling [194]. Because of the distinct characteristics found in these self-cleaning surfaces, including nonwetting and anti-contamination, they may be applicable in a range of situations. Collectively, these new found properties signal a new era in self-cleaning membrane production and application.

Membrane fabrication methods	Challenges and shortcomings
Biomimetic mineralization	Controlled regulation of nanoparticle morphology and surface composition within polymer matrix In-depth analysis of mineralization reaction thermodynamics and kinetics with different inorganic precursors and organic inducers
Biomimetic adhesion	Unambiguous elucidation of formation mechanism and structure of PDA with convincing experimental evidences Long-term stability of PDA coating under extreme working environments
BCP self-assembly	Facile synthesis of well-defined block copolymers for rationally controlling the phase separation process Precise control of defect-free self-assembly process and pore size/morphology
Surface segregation	Synergistic control of the thermodynamics, kinetics, for selective surface segregation Manipulating multiple interactions for hierarchical structure creation

Table 3. Challenges and shortcomings of membrane fabrication methods that imitate the formations found in natural prototypes.

2.4.1.1. Fabrication of membranes via incorporation of low surface energy moieties

Lower surface energies and surface microscale and nanoscale geometrical structures are two of the primary dynamics when it comes to the efficacy of hydrophobic or oleophobic self-cleaning type membranes [195]. The methodologies applied when developing self-cleaning membrane surfaces may be grounded in two specific tactics. The first one requires building a rough surface using low surface energy materials, whereas the other is based on altering the rough surface with materials with lower surface energy values. The process of design and production of the bioinspired superhydrophobic membranes using electrospinning has become a popular research direction. In particular, electrospinning is an adaptable approach for making rough surfaces using low surface energy materials, that depend on this roughness, as hierarchically textured surfaces with microstructures or nanostructures, and added during the process of spinning. Roughness' length scale is credited to the smaller fiber diameters and hydrophobicity and is essential for the superhydrophobicity properties of fibrous membranes. Multiple methods have been noted for combining materials of lower surface energy together with higher surface roughness, including poly (3-phenyl-3,4-dihydro-2H-1,3-benzoxazine) blended with PAN, and electrospinning poly (styrene-*b*-dimethylsiloxane) block copolymers blended with homopolymer polystyrene (PS-*b*-PDMS/PS) [196]. A method based on in-situ was used to produce superhydrophobic fiber mats with the aid of electrospinning polystyrene that contains fluoroalkyl end-capped polymer additives [197]. Unrestricted surface segregation of these additives with respect to the polymer-air interface can generate fibers that have superhydrophobic properties, are fluorine-rich, and show lower surface energy values. Although it is inspired by biological superhydrophobic surfaces offering hierarchical surface roughness characteristics on at least two different length scales, there is a need for a much finer scale structure so as to create a second level of roughness. A number of artificial superhydrophobic microporous and nanoporous fibrous membranes have been produced using an approach that builds a second level hierarchical surface based on nanohybrid systems. Nanomaterials,

like Al_2O_3 nanoparticles, TiO_2 nanoparticles, SiO_2 nanoparticles, and graphene nanoflakes, collect within the polymeric fibers and as a result alter the surface chemistry and morphology, eventually allowing for superhydrophobicity with improved self-cleaning characteristics [198]. For example, an artificial composite fibrous membrane was created with the help of polyaniline (PANI) doped with azobenzenesulfonic acid blended with PS and using electrospinning (**Figure 36**). In this instance, a network of nanofibers with multiple sub-microspheres was spanning over the entire substrate connected with nanoknots, as well as nanoscale protuberances sheltering every sub-microsphere. The hierarchical roughness of microparticles and nanofibers has the capacity to improve the temperature-responsive wettability by switching between superhydrophobicity and superhydrophilicity activated by temperature.

Chemical vapor deposition process is a single-step solvent-free deposition method for surface modifications that may help add lower surface energy properties to nanoscale rough surfaces that can then generate improved hydrophobic self-cleaning membrane surfaces. Superoleophobic as well as super-hydrophobic self-cleaning nanocellulose aerogel type membranes were created with the aid of cellulose nanofibers that have been treated with fluorosilanes through CVD. The superoleophobic and superhydrophobic characteristics were due to the fluorinated fibrillar networks and aggregates with structures occurring at varying length scales. A noticeable improvement in fibrous membranes' hydrophobicity was observed, when CVD was combined with electrospinning [200]. Both, first level of roughness related to the fibers and second level of roughness related to the beads, were present in the poly caprolactone (PCL) fibrous membranes. The substantially lower surface energy in the coating layer produced using CVD allowed for a constant superhydrophobicity with a contact angle of 175° . This double-roughened highly hydrophobic fibrous type membrane was developed through the process of improving micrometer-scale electrospun fibers with nanometer-scale particles or pores [201]. The combination of chemical composition, roughened texture, and re-entrant surface curvature was likewise examined so as to design an oleophobic self-cleaning fabric membrane. Specifically, this membrane relies on the exceedingly low surface energy

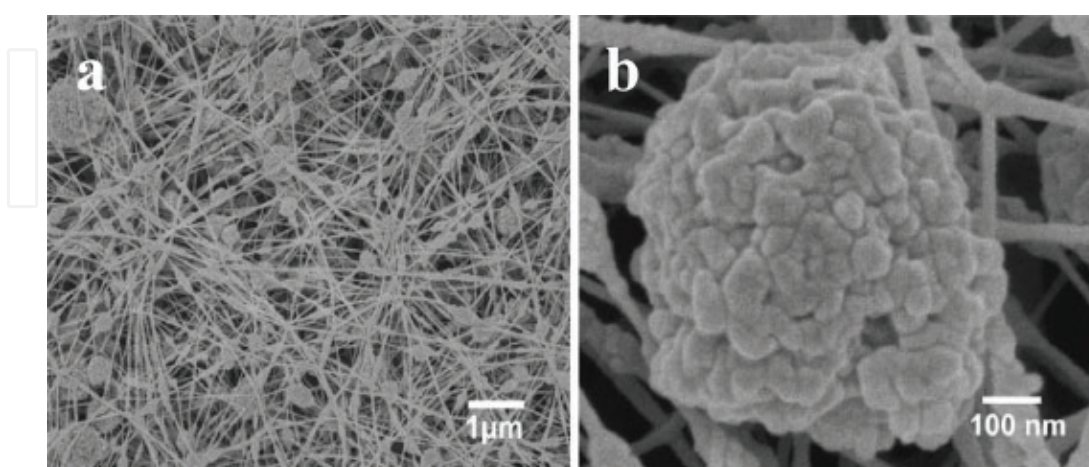


Figure 36. (a) SEM image of an electrospun PANI/PS composite fibrous membrane with lotus leaf-like structure. (b) Magnified view of a single sub-microsphere from (a). Source: Ref. [199], Copyright 2006; reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

polyhedral oligomeric silsesquioxane (POSS) molecules, featuring a rigid silsesquioxane cage enclosed by per fluoro-alkyl groups (fluoro POSS) [201]. A number of experimental oleophobic membranes were created using a straightforward dip-coating and thermal annealing technique that applied a combination of fluoro POSS and PMMA, cross-linked poly (ethylene glycol) diacrylate (x-PEGDA), cross-linked PDMS, or poly (ethyl methacrylate) (PEMA) onto the textured substrates, like stainless steel wire meshes, that have re-entrant curvature on the rougher length scale [202]. For instance, a variety of fabric morphologies with multiple scales of roughness, high porosity, and “beads on a string” type morphology can be adjusted by changing the concentration of the fluoro POSS and PMMA blends [202]. Those surfaces that offer multiple scales of roughness allowed fiber membranes to obtain superhydrophobicity and oleophobicity at higher POSS concentration values and hydrophilicity oleophobicity at smaller POSS concentration values. There are, however, other methods available for the design and fabrication of self-cleaning membranes. For example, textile membranes covered with thiol-ligand nanocrystals, based on the interaction between the VIII and IB nanocrystals and n-octadecyl, can gain super-oleophilic and superhydrophobic qualities [203]. Furthermore, PVDF membranes, made out of linked spherical microparticles that have been uniformly dispersed on the surface, can be produced using an inert solvent-induced phase inversion that showcases superoleophilic as well as superhydrophobic potential [204]. Alternatively, the nanoparticle-polymer suspension coating was applied during the production of a self-cleaning stainless steel mesh membrane [204]. The synergistic effects of the micro/nanoscale hierarchical constructions produced with the help of SiO₂ nanoparticles and the hydrophilic-oleophobic groups of poly(diallyldimethylammonium chloride) (PDDA)-sodium per fluoro octanoate (PFO) allowed the spray-coated mesh membrane to successfully gain superoleophobic and superhydrophilic characteristics. A research study on this subject recently showed how amphiphilic self-cleaning membrane surfaces, that offer low surface energy characteristics and mixed domains of mosaic hydrophilic, were produced using surface grafting per-fluoroalkyl molecules that instigated surface segregation in lower surface energy amphiphilic copolymers [205]. Constructed with fluorine-based polymers, the lower surface energy microdomains located on the membrane’s surface were supposed to decrease the intermolecular interactions occurring between the membrane’s surface and oil. The hydrophilic domains were intended to restrict water molecules and create a hydration layer that would become an oil, water, or solid interface for oleophobicity.

2.4.1.2. Fabrication of membranes via the incorporation of high hydration energy moieties

Research has shown that superhydrophilic surfaces submerged into water can likewise encourage self-cleaning behavior and oleophobicity. The elevated hydration conditions of hydrophilic moieties located on the membrane’s surface have the capacity to restrict a relatively large ratio of water molecules by using hydrogen bond or electrostatic interaction, both of which essentially prevent the oil’s entry onto the membrane’s surface. These approaches to producing underwater hydrophilic or oleophobic self-cleaning type membranes place emphasis on incorporation of high hydration energy moieties onto the membrane’s surfaces. On the other hand, the underwater self-cleaning superoleophobic membranes offer unusual microscale and nanoscale hierarchical structural organizations. Research collaborations have reported underwater

superoleophobic membranes made out of polyacrylamide hydrogel-coated mesh membranes with microscale porous metal substrates and coarse nanostructured hydrogel coatings [206]. A thermal-responsive block copolymer PMMA-*b*-PNIPAAm was casted onto a steel mesh so as to create a membrane that can have two switchable states of wettability depending of temperature values (**Figure 37a**) [207]. A PMMA-*b*-PNIPAAm had undertaken a self-assembly process into a lamellar structure featuring PNIPAAm domains between the hard walls of PMMA on a nanometer scale. In this case, the alternating conformational modification of the PNIPAAm chain establishes the surface roughness at a value near lower critical solution temperature, while the collaboration between PMMA and PNIPAAm domains grants the film reversible switching between wettability conditions of hydrophobicity/oleophilicity and hydrophilicity/oleophobicity (**Figure 37b**). Moreover, underwater superoleophobic chitosan-coated meshes based on cross-linked chitosan network were successfully produced, and the overall stability potential of chitosan-coated meshes may be enhanced through the modification of the CS coating and its reduction, PVA addition, and full cross-linking [208].

Latest experimental research developments have reported the creation of underwater superoleophobic membranes based on PMAPS-*g*-PVDF and PAA-*g*-PVDF [207]. These ultralow oil-adhesion and superoleophobic properties of the PMAPS-*g*-PVDF membrane were caused by the enhanced surface energy and the hydrated conduct of the grafted zwitterionic PMAPS chains whenever in water. A prolonged conformation of hydrated PMAPS chains could incite the creation of a tightly bound hydration layer as well as encourage oil droplets to roll off from the membrane's surface [209]. The PAA-*g*-PVDF membranes' underwater superoleophobic wetting properties were impacted by the hydrophilic nature of PAA chains and the hierarchical micro/nanoscale structure. The micro/nanoscale spherical particles located on the

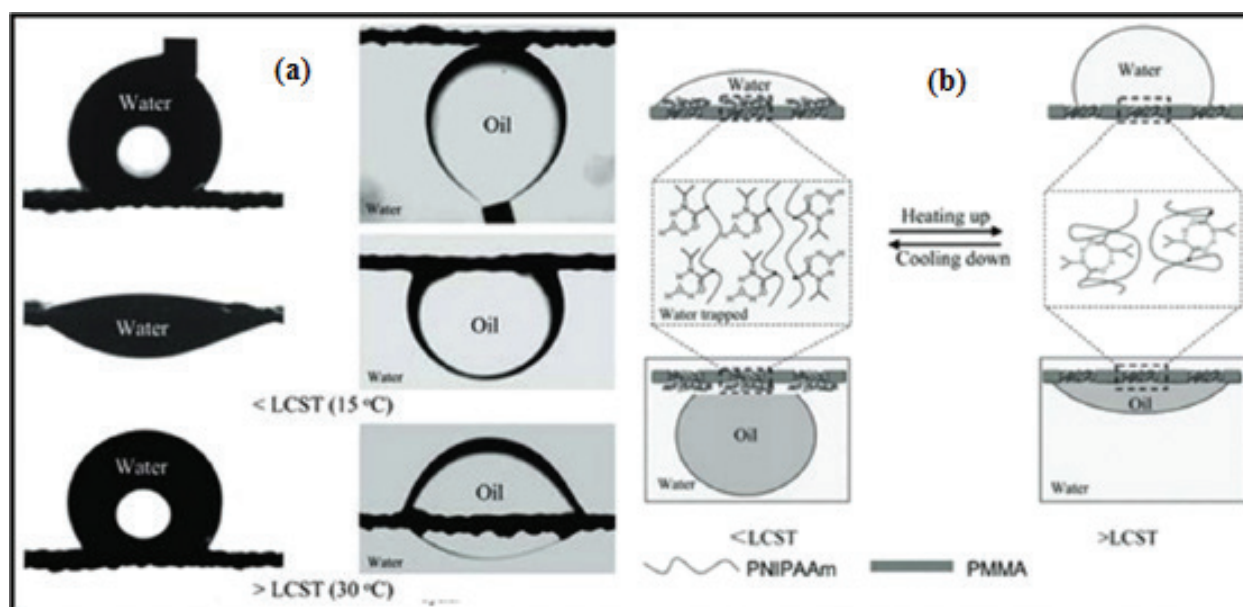


Figure 37. (a) Temperature-controlled water/oil wetting behavior on a block copolymer-coated mesh. (b) A schematic showing reversible conformational change of the PNIPAAm chain and the resultant surface roughness at different temperatures leading to two states of wettability [lower critical solution temperature (LCST)]. Source: Ref. [207], Copyright 2013; reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

membrane's surface were produced using the PAA-g-PVDF micelle aggregates and during the application of the salt-induced phase-inversion method. Specifically, this occurred during the coagulation step, when the quick solvent exchange encouraged the NaCl's crystallization out from the water and the nascent small crystal seeds became accumulation points for aggregates around the PAA-g-PVDF micelles. Thus, this experimental approach was able to illustrate that an increase in roughness can improve antiwetting performance of underwater oils on the membrane's surfaces [210].

2.4.2. Challenges and shortcomings

Researchers that focus on the membrane surfaces' wetting performance have developed key sets of guidelines for the design of self-cleaning membranes. Admittedly, multiple challenges still have to be addressed in this area. When it comes to hydrophobic, or oleophobic, self-cleaning type membranes, the fluorinated moieties were used in the majority of cases in order to decrease surface energy values. The synthesis and application of fluorinated moieties could increase the likelihood of the ecosystem being contaminated by fluorine, which in turn can have a damaging effect on the living organic bodies and materials. As a result, environmentally conscious methods that can address self-cleaning are currently necessary. For the hydrophilic, or underwater oleophobic, self-cleaning type membrane, one of the critical concerns is the strength of the surface hydrophilic quality. Another aspect that has not been adequately investigated is the structural development of hydrophilic layer that experiences intense conditions like higher salinity, alkalinity/acidity, and temperature values. The future of membrane design must shift its focus toward combining strategies that take into consideration multiple interactions and that can significantly improve membrane hydrophilic stability and its applications.

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