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# Applications of Biomimetic and Bioinspired Membranes

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## Abstract

Application fields of the biomimetic and bioinspired membranes are very similar to those of the existing synthetic membranes. Due to the hierarchical structures, as well as controlled selective transport and stability/resistance, the biomimetic and bioinspired membranes have extended applications in sustainable resources, environment, and energy aspects. The most important applications of biomimetic and bioinspired membranes are water treatment, clean energy, carbon capture, and health care.

**Keywords:** sustainability, water, clean energy, fuel cell, carbon capture

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## 1. Introduction

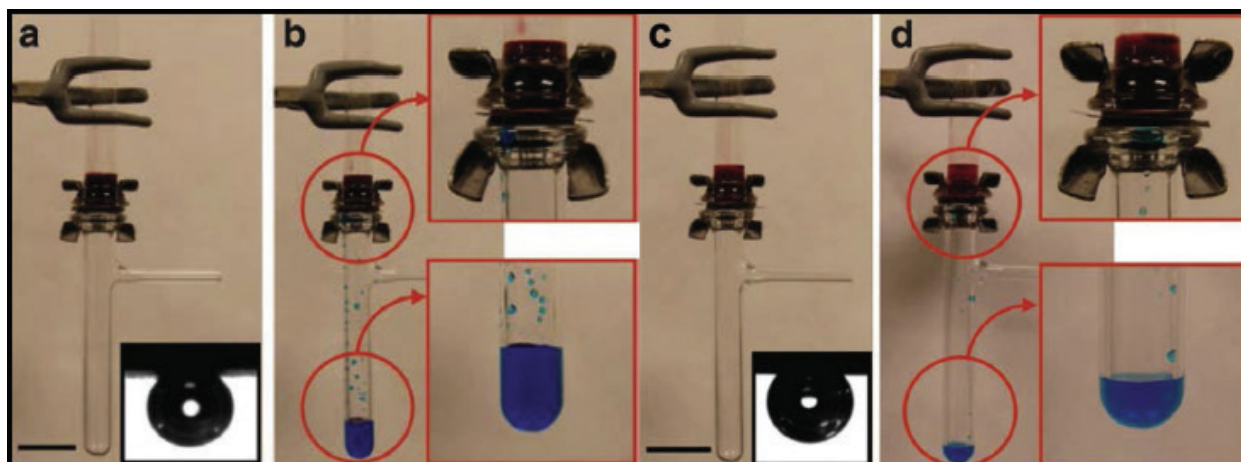
The potential areas for the successful application of the bioinspired and biomimetic membranes are currently overlapping with the ones already taking advantage of and investing into existing synthetic membrane solutions. Because of their implicit hierarchical structures and the controlled selective transport and stability/resistance, bioinspired and biomimetic membranes attract new applications in areas including sustainable resources, energy management, and the environment. However, by far the most relevant areas in which biomimetic and bioinspired membranes can be used are water treatment, health care, carbon capture, and clean energy.

## 2. Water treatment

Global application of biometric membranes in water treatment processes is one of the primary current challenges. The difficulties associated with water treatment processes become a problem

due to the growing amount of wastewater produced from both industrial and municipal sources, and the ways in which these sources have continuously incited concerns with various environmental issues on the global scale. The processes of water purification and wastewater treatment have been designed to allow for the reusing and recycling of discharged water. It is the ultimate aim of the future water reuse facilities and clean water access points to ensure that they can rely upon water drawn directly from the nontraditional sources, including industrial and municipal wastewaters [1]. In the last decade, the application of membrane technology production of high quality water from nontraditional water sources, including agricultural, industrial, municipal wastewater, brackish water, and seawater has been generally accepted. Successful use of filtration membranes has allowed creating the necessary alternative solutions for water scarcity, fresh water supplies, and beneficial reusing of discarded water. Most of the traditional pressure-driven membrane processes, including MF, UF, NF and RO are actively used in industrial and municipal wastewater treatment settings. Currently, there is an additional incentive to integrate next generation high-performance bioinspired and biomimetic membranes for water treatment for industrial and municipal dynamics. Both the diverse parameters and complexity of the water being filtered can incite additional concerns when it comes to membrane used for water and wastewater treatment. Membrane fouling is arguably the greatest issue for a widespread implementation of water treatment membranes, since it contributes to drastic flux decline, increases cleaning requirements, and dramatically raises energy consumption and operating costs. The issue of fouling frequently occurs in water filtration when the water going through the membrane contains foulants such as particles, colloids, macromolecules, hydrocarbon mixtures, microorganisms, and natural organic matter. The additional foulants can be deposited and then adsorbed onto the membrane's surface or its pore walls. This additional deposit can greatly reduce the water flux and detrimentally affect the separation performance of membranes. The bioinspired and biomimetic strategies introduced new ideas for better design and development of a range of antifouling membranes that have the potential to offer an improved separation capacity. Oil-contaminated wastewater produced as a result of hydrocarbon processing, oil-spill mixtures, and metallurgy creates extensive environmental pollution. As a result, it is essential to develop antifouling membranes that would be able to remove oil and other contaminants from water in an effective manner. Research based on the versatility of anchoring properties in mussel and their adhesive proteins has allowed to introduce hydrophilic Polydopamine (PDA) for an improved oil fouling resistance in MF, UF, NF, and RO membranes [2–7]. Freeman et al. [2, 7] placed PDA on PSf support polyester membranes in pressure-delayed osmosis and studied the antifouling ability of PDA-modified membranes used in oil/water filtration processes. The membranes modified with PDA for all dopamine concentrations, deposition times, and alkaline pH values were noticeably more resistant to oil fouling than the PDA-uncoated membranes during emulsified oil–water filtration. The advantages gained from the use of PDA also allowed for a range of reactions with functional organic molecules, such as Michael addition or Schiff base reactions between catechols and amines [3]. Amine-terminated poly(ethylene glycol) (PEG-NH<sub>2</sub>) was anchored onto PDA-modified MF, UF, NF, and RO membranes and improved fouling resistance by taking advantage of the existing fouling resistance properties of PEG [3, 5, 6]. PDA and PDA-g-PEG-modified Polytetrafluoroethylene (PTFE) MF membranes had 20 and 56% higher flux, respectively, than the unmodified membranes 1 h after

starting the process of filtering the emulsified oil/water. The PDA and PDA-g-PEG-modified PES UF membranes increased oil emulsion filtration flux by approximately 35%, if compared to the results obtained from their unmodified counterpart after 1 h of filtration time. NF and RO membranes featuring PDA-modified membranes showed roughly 30–50% greater flux parameters than the unmodified membranes after 1 day of oil emulsion filtration, while the PDA-g-PEG-modified membrane indicated no flux decline during the filtration process. The short-term BSA adhesion decrease was likewise observed in all instances of the PDA-g-PEG-modified membranes, and the overall tendency of the BSA adhesion was lowered with the raise of PEG graft molecular weight [3]. In a separate experimental trial, Freeman et al. [4] showed that PDA and PDA-g-PEG coatings might not be able to successfully control long-term membrane fouling. The traditional oil removing membranes are quickly fouled or often blocked by oil droplets due to their inherent oleophilic potential. The self-cleaning lotus leaves and their unique wettability properties can contribute to the wetting/antiwetting behavior of oil droplets, since they are essential to the design of membranes with low oil fouling potential. Research conducted by Tuteja et al. [8] effectively used oleophobic self-cleaning membranes with re-entrant texture and amphiphilic characteristics in oil–water separation procedures. The superoleophobic and superhydrophilic mesh membranes spin-coated with fluorodecyl POSS and x-PEGDA blend can selectively separate water from a range of oil–water mixtures using only the force of gravity. The membrane oleophobicity of water was the critical parameter for the separation of oil-in-water emulsions. Once the water phase of the emulsion reached the membrane, the PEGDA chains of amphiphilic surfaces would reconfigure and permit water to freely pass through the membrane, while the hexadecane droplets remained collected above the membrane (**Figure 1b**). Membrane oleophobicity occurring in both air and under water is essential for the separation process in water-in-oil emulsions. The PEGDA chains of amphiphilic surfaces begin the process of reconfiguring when the water droplets within the emulsion touch the membrane. In this case, the hexadecane phase remained above the membrane and the water droplets went through the membrane (**Figure 1d**). The test cases using these membranes suggest that they can separate different oil–water emulsions with great efficiency. In both instances, the permeate contained only ~0.1 wt% hexadecane, while the retentate contained only ~0.1 wt% water. Superoleophobic mesh membranes that were spin-coated with x-poly(dimethylsiloxane) (x-PDMS) blend and fluorodecyl POSS could likewise remove >99% of the emulsified oil droplets from a range of oil/water mixtures when triggered by the influence of electric field [9]. The low solid surface energy values and the re-entrant texture of the membrane permitted it to sustain water and hexadecane in the Cassie–Baxter state (superomniphobic) without an involvement of an electric field. Once the electric field was administered, the polar water in the Cassie–Baxter state under gravity transited into the Wenzel state. At the instance when the applied pressure became higher than the maximum pressure that the liquid–air interface could withstand, the water was able to permeate through the membrane whereas the oil became retained. The superoleophobic and superhydrophilic nanocomposite-coated membranes PDDA-PFO/SiO<sub>2</sub> prepared by Yang et al. showcased desirable water permeation and oil repellency behaviors. These membranes had the potential to selectively separate water from oil–water mixtures and at the same time offer good easy-recycling and antifouling parameter potential [10]. The advantages that can be derived from the bioinspired special wettability properties facilitated the successful application of various

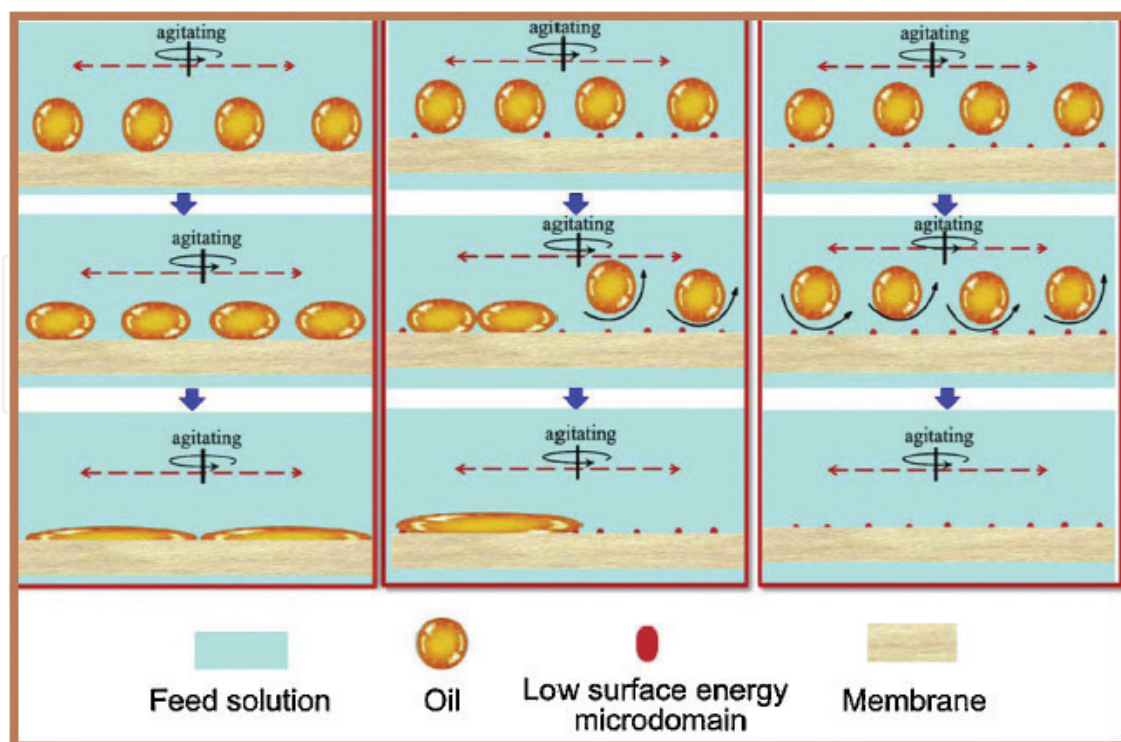


**Figure 1.** Separation of oil-in-water and water-in-oil emulsions. (a) Separation apparatus with a 50:50 (v:v) hexadecane-in-water emulsion ratio above the membrane. Inset, hexadecane droplet on a surface spin-coated with fluorodecyl POSS and x-PEGDA blend, submerged in water containing a dissolved nonionic surfactant. (b) Water-rich permeate passed through the membrane, while hexadecane-rich retentate was retained. (c) Separation apparatus with a 30:70 (v:v) water-in-hexadecane emulsion above the membrane. Inset, hexadecane droplet on a surface spin-coated with fluorodecyl POSS and x-PEGDA blend, submerged in water containing dissolved PS80. (d) Water-rich permeate passed through the membrane whereas hexadecane-rich retentate was retained. Water is dyed color blue and hexadecane is dyed color red. Ref. [8], Copyright 2012; reproduced with permission from the Nature Publishing Group.

superhydrophobic and superoleophilic membranes during the process of oil and water separation [11, 12]. Research group by Ding et al. [13–15] was able to achieve high-throughout separation of oil-water mixtures when they used fluorinated hybrid superhydrophobic and superoleophilic electrospun nanofibers. In this case, the oil–water emulsions or mixtures were poured onto the membranes and the oils quickly spread and permeated through the membranes with the water remaining on the membrane’s surface. For instance, a promising flux of  $3311 \text{ L m}^{-2} \text{ h}^{-1}$  and high separation efficiency potential was noted by researchers [14]. The hierarchical structures of fish scales that allow fish to maintain their bodies clean in oil-polluted water also provide potential ideas for solutions. To illustrate, underwater superoleophobic poly-acrylamide hydrogel-coated [16] and chitosan-coated [17] mesh membranes have been effectively applied in gravity-driven separation process of oil–water mixture where they showed separation efficiency potential higher than 99% for a range of oils. The hydrophilic coatings can absorb water as part of its balanced state in cases with water presence. Once the hydrogel coatings became in contact with the oil droplets, water can become trapped in the coarse nanostructures and the new oil–water–solid composite interface begins to showcase superoleophobic properties. This is caused by the trapped water molecules and the fact that they dramatically decrease the contact area between oil droplet and membrane’s surface with discontinuous triple-phase contact line. Research group of Jin likewise proposed underwater superoleophobic polyelectrolyte-grafted Polyvinylidene difluoride (PVDF) membranes that can effectively separate surfactant-free oil-in-water emulsion with high separation success rate ( $>99.99\%$ ) and high flux potential ( $>1500 \text{ L m}^{-2} \text{ h}^{-1}$ ,  $0.01 \text{ MPa}$ ) [18, 19]. The amphiphilic self-cleaning membranes were created with compositional heterogeneity merging the fouling release property of low surface energy components with the fouling resistance of hydrophilic components on the surface. This self-cleaning membrane was then applied to oil/water emulsion separation [20–23].



The concerns that arise from membrane fouling can be effectively suppressed through dynamics that allow permeation flux to decline to an ultra low level with the smallest value of less than 3.4%, and ensure that after simple hydraulic washing process, the permeation flux recovery is retained at nearly 100%. As part of this vigorous filtration process, the fouling release properties of low surface energy micro domains stopped coalescence, spreading, and migration of the holistic hydrophobic oil droplets. This preventative measure remarkably reduced and even prevented the decline of the reversible flux. The hydrophilic domains improved the antifouling properties even more by creating compact hydration layer and opposing the nonspecific interaction between the membrane's surface and the incoming foulants. Medium levels of applied shear force effortlessly brushed the oil droplets away from the surface and then pushed them back into the rest of the feed solution (**Figure 2**). Alternatively, bioinspired superhydrophobic self-cleaning membranes featuring micro/nanoscale hierarchical structures and displaying very high levels of water repellence could also be used for membrane distillation. Researchers Wang et al. [24] introduced electrospun PS micro-/nanofibrous membranes displaying comparable micro/nanoscale hierarchical structures of silver ragwort leaf and lotus leaf during desalination with the aid of direct contact membrane distillation process. The properties of high superhydrophobicity ( $>150^\circ$ ) helped to prevent membrane wetting and guaranteed high liquid entry pressure for stable low permeate conductivity. The relatively high porosity values ( $\sim 70\%$ ) improved the vapor permeation potential and allowed it to be about 4–5 times higher than the values found in commercial PVDF membranes. The application of the combined fabrication method ensured that the electrospun nanofibers were improved with silver nanoparticle and 1-dodecanethiol with the aid of poly-dopamine acting



**Figure 2.** Illustration of the flux decline resistant mechanism in amphiphilic membranes with compositional heterogeneity [24].

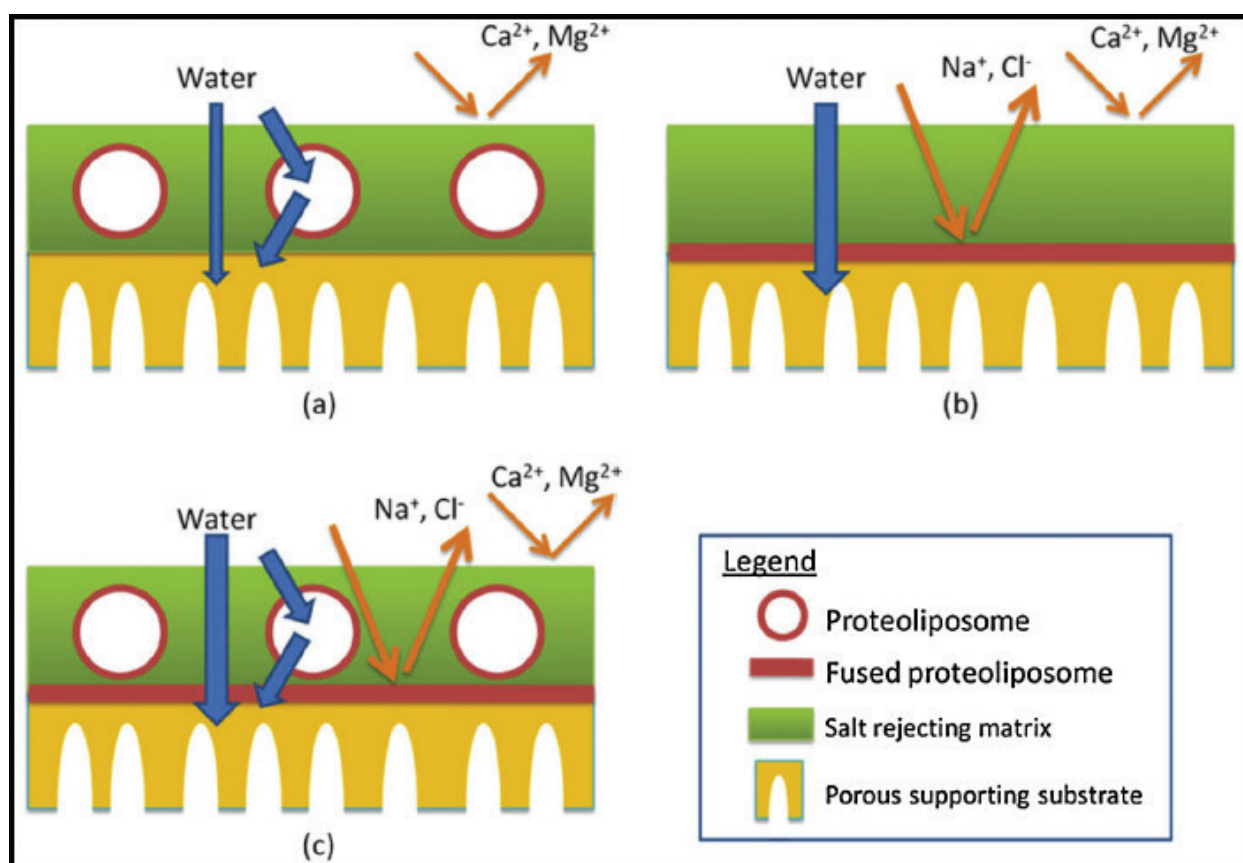
as “bio-glue.” This in turn gave the nanofiber membranes superhydrophobicity caused by the hierarchical structures, since they were advantageous for membrane distillation application process [25]. This substantial water flux enhancement of 2–3 times higher than a commercial PVDF membrane was credited to the open surface pore structure quality, while the stable and low conductivity ( $<5 \mu\text{S cm}^{-1}$ ) was due to the lack of pathways for NaCl that would otherwise allow permeate to pass through the superhydrophobic membrane. Researchers Mansouri et al. [26] noted the heightened antifouling property of superhydrophobic fluorosilanized  $\text{TiO}_2$  nanocomposite PVDF membranes when it came to various concentrations of both humic acid and NaCl solutions. This dynamic suggests a possibility of a long term antifouling performance potential in real seawater environment. A more successful treatment of industrial wastewater types can be achieved through the inclusion of nonfouling polymer brushes onto the membrane’s surfaces. This approach offers a highly promising option for repelling various types of foulants, including hydrocarbons, microorganisms, colloids, and biomacromolecules. Membrane surfaces modified with phospholipid-like zwitterionic materials have been habitually implemented to repel proteins, cells, and other organic compounds from adhering to the membrane’s surface. Research suggests that the zwitterionized PSf membrane based on the PSf/PDMAEMA-*b*-PSf-*b*-PDMAEMA blended membranes are almost without cell adhesion [27]. The PVDF-*g*-PCBMA and PVDF-*g*-PSBMA membranes based on PVDF/PVDF-*g*-PDMAEMA blend membranes showed an absence of protein deposition [28]. The PVDF membranes covered with amphiphilic PPO-*b*-PSBMA were able to successfully repel non-specific protein surface adsorption throughout the dynamic filtration process and featuring minor irreversible flux decline ratio of 4.1% [29]. The zwitterionic colloid particles-coated PSf membranes have been reported as showing positive antifouling properties and facilitating a stable nanofiltration function when confronted with humic acid and BSA in a 30 h of filtration test scenario [30]. In order to produce durable membranes that can maintain stable effluent quality for long-duration water treatment operation, research has been focused towards membranes with self-healable antifouling properties. For instance, natural superhydrophobic plant leaves can self-heal damaged voids in the epicuticular wax layer through the process of rearranging wax molecules into layered structures. This restructuring guarantees the stability of wettability properties over the membrane’s lifetime. Membranes created using surface segregation of amphiphilic copolymer may likewise include the rewarding properties of offering self-healing potential. These self-healing properties occur due to the damaged antifouling brush layers and the fact that eventually they are completely replaced by the surface segregation agents from the membrane’s bulk. This allows for an almost complete recovery of antifouling properties in the membrane. The flux recovery ratio for the surface segregation membrane including zwitterionic SBMA content of 5.8 mol% was noted to be retained at 92%, even after three cycles of protein ultra-filtration [31]. The flux recovery ratio values of the surface segregation membrane featuring near-surface coverage of Pluronic F127 of 62 mol% showed flux recovery potential as high as 90% within three repetitive protein ultrafiltration operations [32]. The low surface free energy membrane surfaces produced using forced surface segregation of fluorine-containing copolymers could similarly maintain more successful antifouling performance capabilities with oily foulants after several cycles of ultrafiltration

operation [20–22]. In a large number of water and wastewater treatment applications, contaminants such as metal ion, bacteria, proteins, and other contaminants polluting the water are removed primarily using the sieving mechanism that relies on the membrane's pore sizes and the size range of its contaminants. Research suggests that nanoporous membranes can be highly useful for the advantageous resolution but also for better capability throughout. Sophisticated selective transport properties of cell membranes helped develop a number of new strategies useful during fabrication of biomimetic and bioinspired membranes able to conduct effective water treatment.

The development of nanoporous biomimetic membranes containing Aquaporins (AQPs) holds a lot of possibilities for water purification applications. AQPs unique permeability and selectivity make these membranes a likely candidate for the design of high-performance membranes intended to be used for desalination. Research conducted by Kumar et al. [33] showed that AQP-incorporated triblock copolymer membranes can help develop significantly more controllable, sustainable, and productive water treatment membranes. These membranes would be able to provide a range of permeability levels, depending on the various concentrations of AQPs used. Research test cases showed that permeability peaked at a protein-to-polymer ratio of 1:50 and featuring permeability 3000 times greater than that of the pure polymer. Methodical studies have been conducted on active AQP-based composite membranes and have suggested relatively competitive water permeability potential and enhanced ion rejection values for existing RO, FO, and NF system [34–44]. An exceptional performance of AQP-based NF membrane can allow for the overall water flux of  $36.6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  and an  $\text{MgCl}_2$  rejection of 95% (1 bar) [43]. In most cases, the AQP-based composite membranes had highly multivalent ion rejection capabilities, however, with a smaller NaCl rejection that restricted its applications for brackish and seawater desalination processes. Multiple innovative approaches for building AQP-based composite membranes with compatible NaCl rejection potential have been reported. Researches Chung et al. [35] cross-linked ruptured AQP-incorporated vesicles with acrylate-functionalized polycarbonate membrane support in order to facilitate a reduction in the number of uncovered pores to an insignificant level and to augment the NaCl rejection to a level above 98.5%. Chung et al. likewise implemented AQP-embedded vesicular membrane stabilized using an optimized layer-by-layer PDA-histidine coating during specific forward osmosis testing mode. This particular form osmosis testing relied on 6000 ppm NaCl as the feed, 0.8 M sucrose as the draw solute, and reporting high salt retention levels of 91.8% [40]. Alternatively, Tang et al. [38] determined that 1,2-dioleoyl-sn-glycero-3-phosphocholine-based proteoliposomes showed highly desirable osmotic water flux and NaCl reflection. They were also able to achieve adequate levels of NaCl rejection ( $\sim 97\%$ ) and excellent water permeability parameters ( $4.0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ) by using AQP-incorporated vesicles in well-established interfacial polymerization. Tang et al. offered a potential future of design criteria for AQP-based composite membranes for the application in desalination process [42]. Their research indicated that AQP-containing proteoliposomes were responsible for providing preferential water pathways in the ion rejection layer (**Figure 3a**), while fused AQP-containing lipid bilayers were in charge of NaCl rejection process (**Figure 3b**). The complex joining of lipid bilayer and proteoliposomes embedded matrix has been forecasted to ensure high water permeability levels and excellent



salt rejection values (**Figure 3c**). Although there have been a number of successful accomplishments in the development of AQPs-based membranes, there are still key limitations to their proper scale up and larger scale applications because of the highly specialized requirements and excessively costly nanofabrication techniques [45]. Furthermore, the overall stability of the AQP-containing proteoliposomes during various extreme seawater conditions must be taken into account. On the other hand, carbon nanotubes (CNT) feature a much more rapid mass transport than the one calculated from continuum hydrodynamics models, such as the aquaporin water transport [46]. Prospective applications of CNT as a selective layer on the membrane's surface used for water treatment can be predicted through an array of high flux molecular channels. Membranes that have ultra high density of uniform molecular size pores and can be effortlessly produced on technical scale would constitute a considerable progress for membrane-based water treatment solutions [47]. The property of self-assembly in block polymers suggests new advantages in the production of nanoporous membranes with narrow pore size distributions, sharp molecular weight cut-off values, and high porosity. These features have influenced how nanoporous membranes have been fabricated using self-assembly of block copolymers to exhibit higher flux values if compared to commercial membranes, as reflected in **Table 1**. These fabricated membranes have superior abilities necessary for the competitive macromolecular separation platform due to the monodispersed pores' superior selectivity, smooth



**Figure 3.** Conceptual designs of AQP-based composite biomimetic membranes. Ref. [42], Copyright 2013; reproduced with permission from the American Chemical Society.

Assemblies	Effective pore diameter (nm)	Water permeability ( $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ )
PS-b-PMMA	~15	~450
PS-b-PMMA	~17	~200
PS-b-PI-b-PLA	~22	~165
PS-b-P4VP	~8	~40
PS-b-P4VP	~19	~850
PS-b-P4VP	~50	~600
PS-b-P4VP	~25, 38	~450, 625
PS-b-PMMA	~1–2	~37
PI-b-PS-b-P4VP	~16–36	~150–850
PS-b-PEO	~20–30	~800
PS-b-P2VP	~8–25	~100–300
PS-b-P4VP	~100	~3200
PS-b-P4VP	~25	~600

**Table 1.** Summary of selective nanochannels in membranes based on block copolymer self-assembly.

surfaces that deter fouling, and high void fraction that permits higher fluxes [48]. Research conducted by Stamm et al. offer an illustration of this type of application. The nanoporous PS-b-P4VP membrane based on the self-assembly of PS-b-P4VP/HABA supramolecular complexes showed monodisperse pore radius of 12.3 nm and a high pore density of  $2.43 \times 10^{14}$  pores  $\text{m}^{-2}$ . These values are responsible for the high Congo red dye rejection (>98%) and rapid pure water flux ( $>600 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ ). Additional zwitterionization and quaternization responses during aP4VP instances improve antibacterial and antifouling properties of membranes [49]. Despite the progress being made, there are still significant research strides when it comes to reducing the pore sizes down to the molecular dimensions for small molecule type of separations and to creating long range, dynamic, and highly selective nanochannels for large-scale production and industrial application.

### 3. Clean energy

The advancement of clean energy projects has invited a lot of interest because of the increasing demands for energy consumption and the growing environmental concerns that often accompany energy use and production. Membrane technology offers high efficiency, green conscious, and energy-saving qualities that can be actively used in clean energy production processes. In fact, membrane technologies show clear economic and technical advantages over many conventional technologies that are not environmentally conscious. Currently, biomimetic and bioinspired membranes are being incorporated into broader research and industrial applications and continue to promise further developments.

### 3.1. Fuel cells

Fuel cells are electrochemical devices that use the reaction between fuel, such as hydrogen, alcohol, or other hydrocarbon compound, and oxidant, or oxygen, to transform fuel's chemical energy into electric energy, but without being processed through the heat engine. For a wide range of fuel cells, the ion exchange membrane is the primary component that defines how well the fuel cell performs its job of conducting ion. Membranes' critical role in fuel cells is to prevent the diffusion of fuel from the anode to the cathode. If the membrane fails to effectively prevent the diffusion, it will dramatically reduce the performance of fuel cell because of the potential mixed effect and electrode poisoning [50, 51]. Different bioinspired and biomimetic tactics have been implemented in order to stimulate ion conduction process and inhibit fuel diffusion. Researchers Xu et al. [52] and Liu et al. [53] applied quaternized polymer to encourage mineralization of the silica precursor during the fabrication of hybrid anion exchange membranes. Once the process of hybridization was introduced, membrane's thermal stability and mechanical strength were enhanced by the stable structure of its inorganic component and the interactions between inorganic and organic phases. These improved parameters can offer a number of relevant benefits to the practical application of fuel cells in research and industrial settings. In this case, the methanol crossover was lowered from  $4.1 \times 10^{-10}$  to  $8.45 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  because of the more tortuous methanol-transport pathway and the lowered free volume that heightened diffusion resistance properties of methanol [53]. Another promising variety of ion exchange membrane is the microphase-separated membrane that can form ion-cluster channels and improve the transport speed of ions. Despite its positive characteristics, this membrane has relatively high fuel permeability that restricts its application [50, 51]. There are a number of methods for reducing fuel permeability and the process of coating a fuel barrier layer has offered one such methodology due to its high efficiency and easy manipulation [54]. The barrier layer has the capacity to block the ion-rich hydrophilic domains in microphase-separated membranes, and as a result prevent the crossover of fuel [51]. However, the ion conductivity can decline if the coating layer is thick and nonconductive [50]. As a result, it is necessary to develop a fuel barrier layer with lower thickness and higher ion conduction capability. Wang et al. [54] relied on the bio adhesion phenomenon when modifying the Nafion membrane surface with PDA, one of the most often used cation exchange membranes with microphase-separated structure. The cross-linking structure of the PDA layer can block the ion-cluster channels and subdue the Nafion membrane swelling. Moreover, PDA's low hydrophilicity had negative effects on the solution of methanol at the membrane's surface. This caused a decrease of the membrane methanol crossover from  $3.14 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  to  $0.65 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . The ultra-thin quality of the PDA layer and the various proton conducting groups, such as amino, catechol, and imino, within the PDA layer forced Nafion membrane to sacrifice some of its conductivity. Recent research has focused on the block copolymers containing hydrophilic and hydrophobic segments as potentially useful for ion exchange membranes. These types of materials can be highly promising since they easily form ordered ion-cluster channels that resemble biological nanopores/nanochannels and can achieve high ion conductivity potential. A range of block copolymers with sulfonic acid and quaternary ammonium groups has been assembled for proton exchange membranes (PEMs) [55–57] and anion exchange membranes [58], respectively. During the process of

creation, the hydrophilic segments form ordered channels with connected sulfonic acid or quaternary ammonium groups, and the hydrophobic segments form high-stable phases as a part of the supporting substrate. The membrane's morphology and the size of hydrophilic channel may be manipulated through a controlled management of the molecular weight, rigidity of each segment, and hydrophilicity/hydrophobicity [55, 57]. Balsara et al. [57] case studies designed PEMs employing poly (styrene sulfonate)-*b*-poly (methyl butylene) (PSS-*b*-PMB) with the width of dry hydrophilic phases ranging from 2.5 to 39 nm. This experimental study showed that the PEMs, with diameters of hydrophilic phases less than 5 nm, had higher water uptake and proton conductivity at greater temperatures if compared to Nafion membranes and the membranes with larger hydrophilic phases. For example, in an instance where the temperature was increased from 298 to 363 K, the water uptake was raised from 72.5 to 74.9 wt.%, while the proton conductivity increased from 11 to 19 S m<sup>-1</sup> for membranes with hydrophilic phase of about 5 nm. Alternatively, membranes with 7 nm hydrophilic phase showed a lowered water uptake from 52.5 to 30.5 wt.%, and a decreased proton conductivity from 8 to 6 S m<sup>-1</sup> using the same experimental parameters. This experimental phenomenon was caused by the capillary condensation that can occur in confined spaces where a suppression of evaporation water is happening. The obtained data offers a promising possibility for the future uses of PEMs at high temperature values. In addition to creating ordered channels through self-assembly of block copolymers, a number of top-down approaches have likewise been investigated for the construction of ordered channels for ion conduction. During these investigations, porous substrates were grafted [59, 60] or infiltrated [61] with poly electrolytes for ion conduction. Researchers Moghaddam et al. [60] constructed a silica membrane with pores sized 5–7 nm and grafted sulfonic acid groups onto the inner surface for better proton conduction. In this case, the maximum silica membrane conductivity is 11 S m<sup>-1</sup>. In order to maintain high conductivity values at low humidity, an ultra-thin silica layer with the thickness and pore size of ~2 nm was placed at the mouth of the nanopores. The membrane's inner surface was likewise customized with sulfonic acid groups for improved proton conductivity. The pore's small size prevented water release process when used in fuel cells. In fact, the proton conductivity values of the two-layer silica membrane could remain constant while the humidity was below 20%; however, the proton conductivity of mono-layer silica membrane started to decrease once the humidity became 50–60%. The proton conductivity values in the two-layer silica membrane were two to three orders of magnitude greater than those of Nafion membranes at low humidity parameters. The rigidity and solvent resistance of porous substrates helped to effectively suppress the swelling of the poly electrolytes in pores, which if left untreated could lead to greater fuel crossover. As a result, the membrane was assessed as capable of advantageous durability in practical research and industrial applications.

### 3.2. Alcohol fuel

Over the last decade, alcohol fuels including methanol, ethanol, propanol, and butanol, produced from biomass have become a subject of research and investment interest because of their potential to offer an environmentally friendly and renewable alternative to fossil energy. When making alcohol-based fuels and specifically during the key process of fermentation, it is essential that the produced alcohol is timely removed because of its inhibitory effects on the



yeast activity [62]. The process of pervaporation is a fitting method for highly efficient removal of alcohol during continuous fermentation because it is simple in operation, poison-free for microorganisms, energy saving, and easy to pair with the main reaction [62, 63]. During the fermentation process, water is likewise produced and is then removed as a part of the crude alcohol product that must be taken out to form high-purified alcohol. The process of pervaporation is a promising method for the separation of azeotropic mixtures, such as water–alcohol mixture, since it is not limited by the vapor–liquid equilibrium. Both water-permselective and alcohol pervaporation membranes can be implemented during the production of alcohol fuel. At this point in research, various biomimetic and bioinspired strategies have been actively used to generate membranes with greater separation performance that would reinforce the competitiveness of pervaporation method. When it comes to membrane separation processes, the permeation flux embodies the membrane’s treatment capacity and effectually implies that high permeation flux values can lower the required membrane area and decrease investment membrane costs. Research has distinctly shown that the membrane’s thickness can have a direct influence on the permeation flux capacity of pervaporation membranes. Specifically, thin membranes can reduce the diffusion pathway of the permeate molecules and augment membrane’s permeation flux [64]. As a result, composite membranes involving a thin dense separation layer and a thick porous support layer formed using different materials are usually implemented in industrial-scale applications. To further reduce the separation layer’s thickness so to enhance the permeate flux at a given applied pressure, the separation layer needs to be more durable; and a better bonding between the separation layer and the support layer is also desirable. For instance, bioadhesives and biomimetic adhesives, such as CP [65], polycarbophil calcium (PCP) [66], hyaluronic acid [67], dopamine [68], and gelatin [69] have been used for the creation of an intermediate layer or separation layer in composite membranes implemented for the process of ethanol (aqueous) solution dehydration. In research studies using CP and PCP as intermediate layers [65, 66], there was a notable change so far as the interfacial strength and interfacial compatibility were enhanced. Based on this research, composite membranes with thin and intact separation layers were successfully generated. Once an intermediate layer was added, the separation factor of composite membranes was raised by more than one order of magnitude and indicated the presence of advantageous long-term operational stability. Specifically, the membranes employing PCP as the intermediate layer exhibited an exceptional separation performance with the permeation flux of  $1.39 \times 10^3 \text{ g m}^{-2} \text{ h}^{-1}$  and the separation factor of 1279. Membranes generated using self-assembly of diblock or triblock copolymers has incited considerable interest in pervaporation because of their capability to provide continuous phase for the permeate transport process. PDMS [62] and polybutadiene (PB) [62, 70, 71] are commonly used for transporting blocks for ethanol-selective membranes. Researches Balsara et al. [62, 70] and Buonomenna et al. [71] examined the effects of molecular weight, as well as solvent and mass ratio of various blocks, on the ethanol/water separation performance and morphology of block copolymer membranes. A continuously growing molecular weight of block copolymers caused larger domain spacing and acted in a manner that improved the permselectivity of ethanol [62]. Both the solvent [71] and mass ratio of blocks [70] had a substantial effect on the self-assembled morphology, including spherical, lamellar, and cylindrical morphologies. Notably, the continuous cylindrical morphology showed the

best separation performance. During a test featuring this type of membranes and fermentation broth as the feed solution, the results produce an enrichment of ethanol from 8 to 40 wt.% [70].

### 3.3. Clean gasoline

In the forthcoming years, fossil fuels will still continue to play a central role in the production of heat and power for daily life and industrial environments. As a result, the process of cleaning fossil fuels remains a critical strategy that can help curtail environmental pollution and its extensive implications. Sulfur compounds within the gasoline are the primary sources of atmospheric pollution and acid rain. These compounds are also poisonous catalysts of the vehicle exhaust gas convertor [72]. As a consequence, the sulfur compound content in gasoline must be strictly controlled and enforced. Over the last decade, the process of pervaporation desulfurization has received increased attention because of its various benefits over conventional hydrodesulfurization processes. Some of these advantages include higher selectivity, lower operating costs, decreased energy costs, facile scale up, easier maintenance of the octane number, as well as without hydrogen source and coproduct of  $H_2S$  gas [72–74]. Several bioinspired and biomimetic strategies have been implemented for the development of membrane materials with superior separation stability and performance potential. PDMS is used as the primary membrane material for pervaporation desulfurization of gasoline due to its superior processability, greater permeability, and high affinity for sulfur components. Despite these numerous advantages, pure PDMS membranes suffer from low strength and selectivity because of their highly flexible molecular chains [72, 73]. It has been noted that the appropriate incorporation of inorganic materials in polymeric matrix can in fact enhance the physicochemical stabilities and mechanical properties of the membrane. These hybrid membranes have the capacity to overcome the trade-off obstacle between selectivity and permeability effectively manipulating membrane's hydrophilicity/hydrophobicity and the arrangement of polymer chains that influence the entire chain spacing and chain rigidity values [75, 76]. PDMS– $SiO_2$  hybrid membranes were generated using the in situ biomimetic mineralization method [72, 73]. These membranes show that the utilization of silica precursor with greater reactivity values can contribute to the formation of smaller silica nanoparticles. As a result of this formation, a larger interfacial area caused more hydrogen bonds to occur between the silanol groups on the silica surface and the oxygen atoms on the polymer chains that in turn substantially improved the mechanical strength potential of the membranes. The infusion of silica into PDMS matrix is likewise helpful for increasing number and size of free volume cavities, a dynamic that actively supports lower diffusion resistance to the penetrant molecules. The prepared hybrid membrane displayed an exceptionally good desulfurization performance with a permeation flux of  $10.8 \times 10^3 \text{ g m}^{-2} \text{ h}^{-1}$  and a selectivity of 4.8 toward thiophene in gasoline model.

The high cohesive/adhesive energy properties of bioadhesives contributed to the preparation and incorporation of dopamine nanoaggregates into PDMS matrix [77]. Once the dopamine nanoaggregates were added, the chain rigidity and cohesive energy of PDMS were improved, as well as its thermal stability and swelling resistance. The free volume properties of PDMS membrane were similarly optimized through the intervening of dopamine nanoaggregates during the packing of PDMS polymer chains. The simultaneous improvement of permeation flux and enrichment factor was obtained when permeation flux increased from  $2.78 \times 10^3$  to

$6.90 \times 10^3 \text{ g m}^{-2} \text{ h}^{-1}$  and enrichment factor grew from 4.3 to 4.5, thus surpassing the upper-bound curve of the PDMS control membrane. Researchers Jiang et al. generated an ultra-thin PDA coating on the PSf substrate. If compared to the PDMS membrane properties, the PDA membrane showcased higher hydrophilicity, higher cohesive energy, lower thickness, and higher adhesive strength with PSf substrate. Furthermore, this improved the PDA/PSf composite membrane and allowed it to have a more favorable pervaporation performance and long-term durability potential. Double amounts of PDA coating or even more than that were required for the pervaporation desulfurization process since the single-coated PDA showed relatively low selectivity toward thiophene. In addition to the PDMS, PEG can also act as an appropriate membrane material for pervaporation desulfurization of gasoline in accordance with the methodology outlined in the solubility parameter theory. Kong et al. [74, 78] created PEG-b-PAN membranes based on dispersed PEG micro domains and bulk PAN phases. In this case, an increase in the total flux and a decrease in sulfur enrichment factor were attained by either lowering PEG molecular weight or by increasing PEG mass content value that caused greater proportion of PEG micro domains. Additional research is necessary in order to comprehensively study pervaporation desulfurization permeability of PEG-based block copolymer membranes and their various applications in the industrial and environmental projects.

#### 4. Carbon capture

Scientific research has confirmed that the global growth of greenhouse gas emissions in the atmosphere and particularly  $\text{CO}_2$  emissions has acted as one of the key sources in the ongoing climate change over the past several decades. In 2014,  $\text{CO}_2$  accounted for almost 80.9% of all U.S. greenhouse gas emissions caused by human activities. Carbon dioxide is naturally present in the Earth's atmosphere as a part of its carbon cycle, where the carbon naturally circulates between the atmosphere, oceans, soil, animals, and plants. Research prognosis suggests that the  $\text{CO}_2$  emissions are going to severely increase in the foreseeable future [79, 80]. In fact, the International Panel on Climate Change predicts that ice-melt will offer drastically higher projections of between 2.4 and 6.2 feet sea level rise by 2100, because of the increasing of  $\text{CO}_2$  emissions [80]. As part of the solution for resolving this global dilemma, technologies for obtaining  $\text{CO}_2$  from gaseous mixtures can be divided into three specific categories, namely liquid absorption, solid adsorption, and membrane separation [80]. If compared with liquid- and solid-oriented types of technologies, the membrane separation technology offers a series of inherent advantages. Membrane separation is an environmentally friendly process without hazardous chemicals, simple in operation, requiring small equipment and low energy consumption. Substantial research projects have been dedicated to manufacturing high-performance robust membranes using biomimetic and bioinspired strategies for the development of membrane-based carbon capture technology. In fact, the adhesive capacity and iron-fortified property of marine adhesive proteins have been used for membrane design. For instance,  $\text{Fe}^{3+}$ -dopamine organometallic nanoaggregates ( $\text{Fe}^{3+}$ -DA) were integrated into polymeric matrix as a filler in order to construct defect-free and ultra-thin hybrid membranes [81]. In this instance, the interfacial interaction between filler and polymer matrix was optimized by varying the molar ratio of  $\text{Fe}^{3+}$  to DA. This gave the membrane favorable free volume that

was beneficial to the selective diffusion of CO<sub>2</sub> molecules within the membrane. There was a substantial improvement in CO<sub>2</sub>/CH<sub>4</sub> selectivity values from 21 to 72, while the comprehensive performance exceeded the most recent upper bound line. Moreover, the membrane attained a positive suppression of CO<sub>2</sub>-induced plasticization at high operating pressures. The process of self-assembly of block copolymer into a membrane with highly ordered and continuous structure can be an advantage for mass transport through the membrane and has been researched for applications in CO<sub>2</sub> separation and capture. Researchers Cohen et al. [82] interrogated the permeation of gases through PS-*b*-PB block copolymer membranes featuring highly oriented lamellar microstructure. The results obtained by Cohen et al. suggest that the highest permeability was achieved when the lamellae were oriented in a position parallel to the permeation direction. An analogous dependence of permeability on the direction of lamellae orientation was noted by Kofinaset al. [83]. Recent research project by Gao et al. [80, 83] synthesized block copolymers with PS segments and linear PEO or brush-type PEO (poly [oligo (ethylene glycol) methyl ether methacrylate], POEGMA) segments. After the process of self-assembly, cylindrical structures were formed for both BCPs with PEO cylinders oriented perpendicularly to the surface. The perpendicular channel and the ether oxygen linkages in PEO segments were in support of CO<sub>2</sub> permeation. Specifically, the brush-type PEO segments featured lower crystallinity properties if compared to linear PEO segments. These properties afforded the cylindrical channels with high CO<sub>2</sub> affinity and free volume, thus aiding the solution and diffusion properties of the CO<sub>2</sub> molecules. As a consequence, the membrane showed an exceedingly high CO<sub>2</sub> permeance levels of  $5.92 \times 10^{-7} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and an extensive separation performance that surpassed the Robeson's upper bound line. As an enzyme that exists in many organisms, carbonic anhydrase (CA) plays a critical role in the transport of CO<sub>2</sub> in vivo. It is by far the quickest catalyst for CO<sub>2</sub> hydration and dehydration processes as it features a turnover rate of 106 mol CO<sub>2</sub> mol<sup>-1</sup> CA s<sup>-1</sup> and can be used at low CO<sub>2</sub> concentration values [84]. With high levels of catalysis effectiveness, CA-immobilized membranes have been widely implemented for the CO<sub>2</sub> separation process [85, 86]. Researchers Zhang et al. [85] have created a hollow fiber membrane reactor by embedding CA in hydrogel that showed great performance with CO<sub>2</sub>/N<sub>2</sub> selectivity of 820, CO<sub>2</sub>/O<sub>2</sub> selectivity of 330, and CO<sub>2</sub> permeance values of  $3.70 \times 10^{-10} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ . To circumvent the CA inactivation at the industrial-scale production level, Wang et al. [87] generated a biomimetic poly(N-vinyl imidazole)-zinc (PVI-Zn(II)) complex so as to simulate the active site of CA (a Zn(II) tetrahedral center bound to three imidazole residues and a hydroxyl) and obtain a high-performance membrane for the separation of CO<sub>2</sub>/N<sub>2</sub>. The essential effect of PVI-Zn(II) complex on CO<sub>2</sub> hydration reversibly was carefully verified using a varying molar ratio of PVI/Zn(II), pH value of the PVI-Zn(II) solution, and by replacing PVI with polyvinyl pyrrolid (PVP), which significantly changed the structure and the amount of the complex. The CO<sub>2</sub> permeance and CO<sub>2</sub>/N<sub>2</sub> selectivity of PVI-Zn(II) complex membrane were determined to be close to three and two times higher than those of pure PVI membranes, respectively.

## 5. Health care

Health care is becoming one of the most viable fields for the application of innovative membrane technology. New membrane technologies are being used in a wide range of health



care areas, including in diagnosis, prevention, treatment of disease, injury, and other physical and mental impairments in humans. In particular, bioinspired and biomimetic membranes are being implemented in health care and research centers during the design and creation of effective artificial organs, such as artificial kidney, lung, and liver. In addition to excellent selective permeation properties and antifouling performance, the specific requirement for membranes utilized in artificial organs is the compatibility of the membrane's surfaces with its immediate surroundings, such as cytocompatibility and hemocompatibility [88, 89]. Currently, multiple biomimetic and bioinspired methods have been used to construct highly compatible surfaces by immobilizing natural or synthesized macromolecules on the membrane's surface. PVP is a hydrophilic polymer with a highly advantageous biocompatibility that exceeds all the ones available for use as blood plasma substitutes. Zhao et al. [88] altered the PES membrane surfaces with PVP by applying surface segregation of amphiphilic triblock copolymer PVP-*b*-PMMA-*b*-PVP. If compared to the PES membranes, the membranes modified by Zhao et al. offered an improved hemocompatibility (BSA adsorption decreased from 19 to 10  $\mu\text{g}/\text{cm}^2$ , platelet adhesion decreased from  $25 \times 10^7$  cells/ $\text{cm}^2$  to nearly zero, blood coagulation time increased from about 55 to 90 s) and cytocompatibility, with more flat cell morphology, higher surface coverage, and favorable cell viability. These enhancements invested the membranes with a promising potential in the field of blood purification, including hemodialysis and artificial liver production and maintenance. Heparin is a widely used blood anticoagulant with remarkable cytocompatibility, hemocompatibility, and cell proliferation properties [90, 91]. For the grafting of heparin [90–92] and heparin analogs [91] onto the membrane's surfaces, biomimetic adhesion method was employed as a relatively quick, green conscious, and highly effective option relying on coating dopamine-anchored heparins or precoating PDA followed by grafting heparin onto the surfaces. As an alternative to the PVP-modified membranes, the dopamine-heparin-modified membranes showed a noticeably greater improvement in the anticoagulation performance, with clotting time amplified from 10 to more than 60 min for PE/dopamine-heparin membranes [90]. Furthermore, the improved water flux (from 371.4 to 644.9  $\text{L m}^{-2} \text{h}^{-1}$ ) [90], discernably suppressed adhesion, activation, and transmutation of platelets, and helped cell attachment and growth on membrane's surface [90, 91]. These results were the result of an increased surface hydrophilicity and biological activities of heparin molecules. In comparison to the highly complex processes and excessive costs of extracting heparin from the animal body, synthesized heparin analogs have comparable functions and structure of heparin, making it definitively more appealing for practical applications in health care. For example, phosphoryl choline is a biological zwitterion situated on the cell membrane's outside surface and that can offer critical antifouling properties to the cell membrane. It also features encouraging biocompatibility because of its zwitterionic nature and electrostatically induced hydration properties [89]. During the last decade, surface modifications using phosphorylcholine and other zwitterions have been widely examined in an attempt to enhance biocompatibility of the membrane's surfaces [27, 28, 93–99]. Chang et al. [93, 94, 96] examined the hemocompatibility of zwitterionic surfaces by grafting poly(sulfobetainemethacrylate) (PSBMA) onto the membranes. In this case, the optimum antifouling (low protein adsorption), anticoagulant (long plasma-clotting time), and antithrombogenic (low hemolysis of red blood cells solution) properties were obtained once

the membrane's surface had the greatest hydration capacity and the lowest charge bias values. To sum up, the PSBMA-grafted membranes can provide highly desirable nonbioadhesive characteristics when in contact with tissue cells and bacterial medium. They also offered properties that make it a suitable micro environment for skin wound healing, and have been identified as having great potential applications in the rational design and quick preparation of advanced wound dressings [96]. Although more research needs to be conducted on the long term applicability of these membrane approaches, the surface zwitterionization appears as one of the most advantageous strategies for constructing biocompatible surfaces because of its consistently high-rate performance, great diversity, and easy processability properties.

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