



Recent progress in molecular engineering to tailor organic-inorganic interfaces in composite membranes

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This minireview provide an overview of the most recent progress in interfacial molecular engineering of organic-inorganic composite membranes to enhance interface compatibility and promote membrane performance in separation and purification processes. We discuss three typical models, including mixed matrices, interface composites, and dual-layer composites, to demonstrate the design principles of interfacial interactions during different fabrication processes, and summarize valuable strategies to modify the inorganic components and/or polymer matrix. Such composite membranes have applications in water treatment and desalination as well as in other arenas such as batteries and fuel cells. While this review focuses on organic-inorganic composite membranes, similar molecular engineering strategies can be applied in the fabrication and regulation of other composite materials.



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Recent progress in molecular engineering to tailor organic-inorganic interfaces in composite membranes

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Organic-inorganic composite membranes are of great interest in modern water treatment processes because they offer potentially superior separation efficiency and advanced functionality by integrating the properties of polymers and inorganics. The biggest challenge in the fabrication and applications of organic-inorganic composite membranes is the incompatibility of organic-inorganic interfaces. In this minireview, we summarize the most recent advances in molecular engineering to tailor the properties of interfaces in composite membranes. Three typical models (i.e. mixed matrix model, interface composite model, and dual-layer composite model) are presented to demonstrate how to regulate these interfaces via molecular engineering and how the interfacial properties ultimately affect the membrane performance.

1. Introduction

As a vital component in modern separation processes, membranes have been widely implemented in water treatment and desalination facilities to alleviate mounting global water crises.¹ Tremendous progress in membrane manufacturing has been achieved over the past decades to promote pressure-driven (e.g. nanofiltration and reverse osmosis), thermo-driven (e.g. membrane distillation), and electro-driven (e.g. electrodialysis) membrane processes.²⁻⁴ Commercial membranes can be categorized into ceramic membranes and polymeric membranes. Polymer membranes generally have merits of low cost, tunable porous structure, and scalability, whereas ceramic membranes often exhibit superior hydrophilicity and structural stability.⁵ Moreover, some inorganics exhibit advanced catalysis and affinity-adsorption activities.^{6,7} Therefore, organic-inorganic composite membranes have emerged to integrate the advantages of organic and inorganic materials, achieving an optimal membrane performance or coupling advanced functions for efficient separation. Because of the material and structure diversity of polymer membranes, they often serve as the matrix (or skeleton) of organic-inorganic membranes, and the inorganics are blended in the matrix or composited onto the membrane surface.⁸

The concept of organic-inorganic membrane can be tracked back to 1970s. Mineral fillers (e.g. silicon oxides, aluminium oxides and montmorillonite) were added into cellulose acetate (CA) casting solution to improve the compaction resistance.⁹ Since 1980s, the organic-inorganic membranes based on porous inorganic fillers were applied in gas separation,¹⁰⁻¹² and then the hybrid membranes prepared by sol-gel process were developed.¹³ The inorganics can enhance the membrane rigidity for better separation. Meanwhile, some hydrophilic inorganics like ZrO₂¹⁴, TiO₂¹⁵, and Al₂O₃¹⁶ were embedded into polymer matrix to improve membrane permeability. More recently, multitudinous nanomaterials (e.g. graphene oxides (GOs)¹⁷, carbon nanotubes (CNTs)¹⁸, mineral nanoparticles (NPs)¹⁹ and Mxene²⁰) were blended with polymer matrix or composited onto the membrane surface for promoted performance or multi-functions.

Distinct from organic-inorganic hybrid membranes with molecular-scale mixing, microscopic organic-inorganic interfaces can be found in organic-inorganic composite membranes, and the compatibility of these interfaces is challenging during their fabrication and application. According to thermodynamics principles, poor interfacial compatibility will lead to severe aggregation of organic or inorganic components, reducing the mechanical strength of membranes, destroying the pore structure, and compromising stability and durability during long-term operation. To address these issues, molecular modification is normally conducted to promote compatibility of the organic-inorganic interfaces. Surface modifications can further improve membrane performance such as by enhancing flux and fouling resistance.^{21,22}

In 2016, we presented a comprehensive review on surface and interface engineering of organic-inorganic

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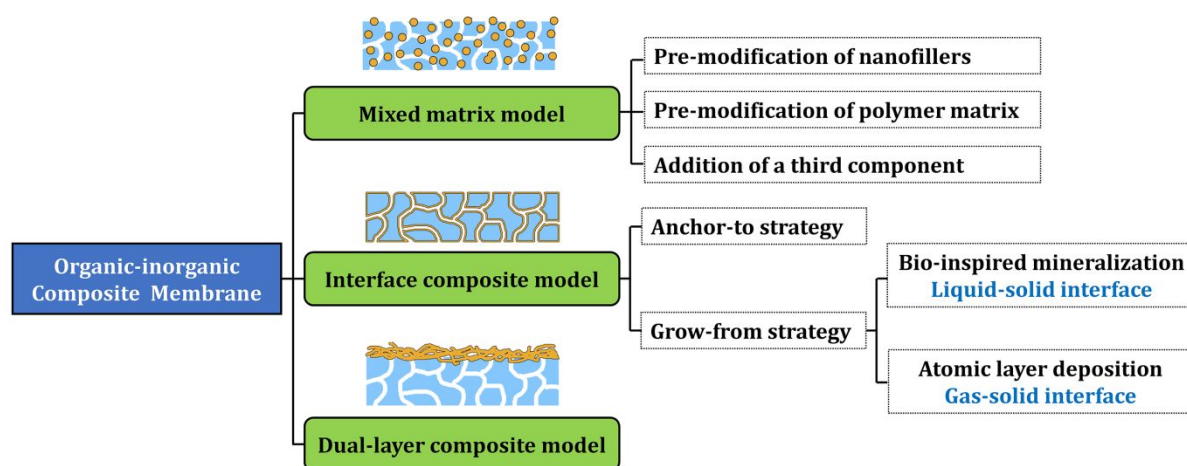


Fig. 1 Models of organic-inorganic composite membranes and their fabrication strategies.

composite membranes. Here, we are updating this perspective by outlining the most recent advances in this field, focusing on organic-inorganic interfaces from the view of molecular engineering. Three typical models of organic-inorganic membranes, i.e. mixed matrix model, interface composite model, and dual-layer composite model are discussed, and the interfacial engineering principles for each model are presented in the following sections (Fig. 1). We hope this review will be a guide for membrane researchers, and, moreover, the interface molecular engineering strategies outlined herein can be also extended to other composite material fabrication fields.

2. Molecular interfacial engineering in mixed matrix membranes

The most direct way to fabricate an organic-inorganic composite membrane is to blend two components and cast the mixture on an interface. However, poor compatibility arising from the polarity differences between inorganic nanofillers and polymers normally leads to nanoparticle aggregation. Specifically, the incorporated particles are usually highly polar because of abundant polar moieties on their surface, while some commercial polymer membranes, such as polyethylene (PE), polypropylene (PP), and polytetrafluoroethylene (PTFE), have a nonpolar nature. One strategy to improve the interfacial compatibility is to eliminate the undesired “differences” between the inorganic component and polymer matrix, representing one of the most important targets of molecular engineering for organic-inorganic interfaces. Moreover, through molecular interfacial engineering, the composite membranes can acquire superior performance and function.

2.1 Pre-modification of nanofiller

One of the most popular strategies to promote organic-inorganic interfaces is surface modification of inorganic nanofillers. Some researchers have modified nanofillers with

functional moieties for better compatibility or enhanced performance. In early research, modified inorganics such as Al_2O_3 , SiO_2 and TiO_2 nanoparticles were incorporated into the membrane matrix for better performance. Recently, nanomaterials such as CNTs and GOs receive great attention in organic-inorganic composite membrane fabrication. For instance, an early research presented by Badawi functionalized multiwalled CNTs (MWCNTs) with carboxyl groups to improve their dispersion in CA membrane, which promoted the water purification performance of the composite membrane.²³ Ayyaru et al. functionalized GOs with sulfonic acid groups, and blended them with polyvinylidene fluoride (PVDF) and polyvinylpyrrolidone (PVP) to fabricate a sulfonated GO (SGO)/PVDF composite ultrafiltration membrane through a conventional phase inversion process.²⁴ Compared to the pristine PVDF and the unmodified GO/PVDF composite membranes, both permeability and anti-fouling property of the obtained membranes were significantly improved due to the substitutional sulfonic acid groups with a robust and thick hydration layer. Moreover, permeability achieved significant improvement under a relatively low amount of SGO, avoiding aggregation of the filler. Besides, silane coupling agents terminated with functional moieties, were mostly used ones to modify the inorganic fillers in the previous mixed matrix membranes. These coupling agents could interact or react with polymer matrix, creating linkages between the fillers, like zeolites, with the matrix.²⁵⁻²⁷

Beyond moiety modification, another common strategy is to graft polymer chains onto the particles to promote interfacial compatibility or endow with novel functionality. As illustrative examples, poly(methylmethacrylate) (PMMA) was grafted on inorganic NPs because of its good compatibility with PVDF,²⁸ and polyhydroxyethylmethacrylate (PHEMA) has served as a grafted polymer in polyethersulfone (PES) and polysulfone (PSf) composite membrane formation.²⁹⁻³¹ Other polymer chains such as poly (acrylic acid) (PAA), hyperbranched

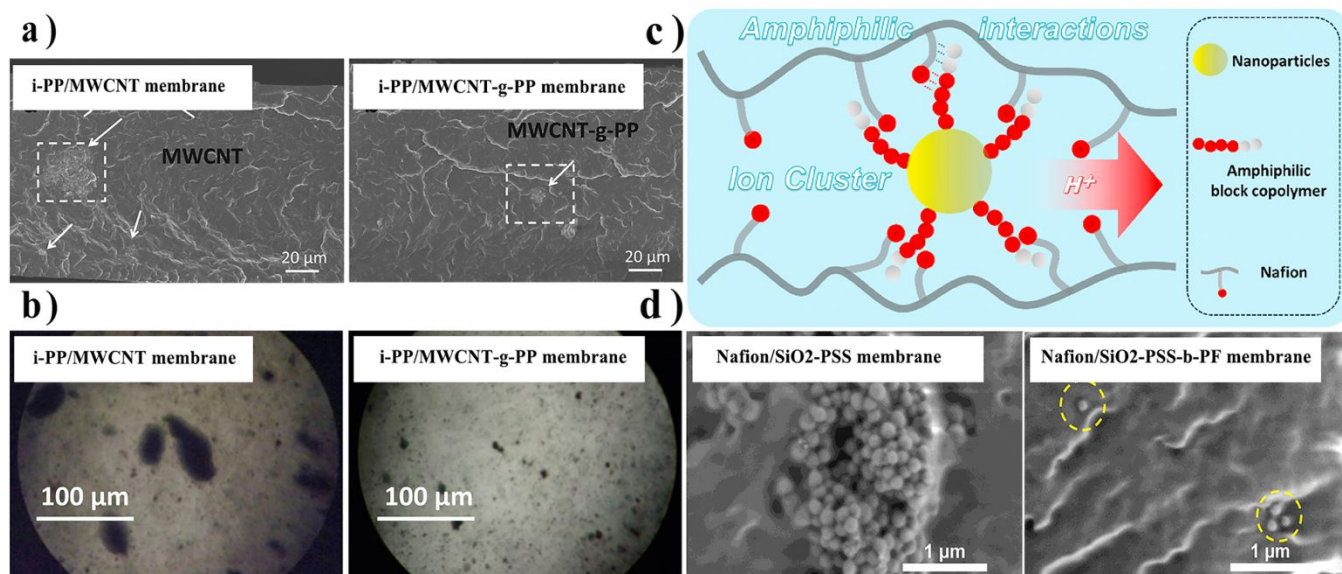


Fig. 2 a) Cross-sectional SEM images and b) optical micrographs of i-PP/MWCNT membrane and i-PP/MWCNT-g-PP membrane. c) Schematic illustration of the interaction between Nafion and amphiphilic block copolymer grafted nanoparticles. d) Cross-sectional SEM image. Reproduced with permission from ref. 36 and 38. Copyright 2017, 2018, Elsevier.

poly (amine-ester) and polyethyleneimine (PEI) were also grafted onto nanofillers to improve the dispersion in mixed matrix membranes.³²⁻³⁵

The polymer component in membrane matrix will, clearly, show the best compatibility with itself, so some researchers have grafted the matrix polymer onto the nanofillers. For example, Bounos et al. blended PP-grafted multiwalled carbon nanotubes (MWCNTs) with isotactic PP to fabricate a mixed matrix membrane.³⁶ The grafted PP chains have the same characteristics as the isotactic PP matrix, which virtually eliminates the distinction between the particles and the polymer matrix and remarkably promotes their compatibility. The water vapor permeability of the composite membrane was selectively enhanced, which was attributed to the good dispersion of MWCNT with the surrounding matrix interphase region. (Fig. 2a, b) However, in most cases, the target of blending nanofillers is to improve the hydrophilicity of membranes, and surface grafting might mask the intrinsic properties, such as hydrophilicity of the nanofillers.

A creative solution to this challenge is to graft amphiphilic block copolymer chains to the NPs. In these systems, the non-polar block is compatible with the matrix, while the polar block provides hydrophilic groups for enhancing membrane performance.³⁰ Ag NPs were pre-modified with amphiphilic polyacrylonitrile (PAN)-co-PAA to fabricate an antifouling ultrafiltration membrane.³⁷ He et al. modified SiO₂ NPs with sulfonated polystyrene-*block*-polyperfluoroallylbenzene (PSS-*b*-PF), and blended them with Nafion to prepare a mixed-matrix polyelectrolyte membrane.³⁸ The Nafion, to some extent, is also amphiphilic because of its hydrophilic -SO₃H and hydrophobic fluorinated chains, reflecting the relationships of the copolymer grafted on NPs (Fig. 2c). The similar properties facilitated the assembly of NP and Nafion

(Fig. 2d), which also promoted the reorganization of ion clusters.

As mentioned above, beyond enhancing interface compatibility, some surface grafting is intended to promote membrane performance. Zwitterionic polymer-modified MoS₂ nanosheets were synthesized and blended into a PES-based composite membrane.³⁹ In this example, MoS₂ sheet served as a carrier to bring hydrophilic zwitterionic polymer into the membrane for enhanced flux, while the MoS₂ itself could also adjust the sieving property of the membrane. This molecular engineering is similar to the modified SiO₂ NPs mentioned above, in that it not only improves the interfacial compatibility but also endows the membranes with other synergistic effects.

In contrast to surface grafting and moiety modification, functionalizing nanofillers with a third nano-sized inorganic component by in situ generation/growth, is an emerging strategy, providing a tunable and efficient approach to reducing agglomeration and enabling advanced functionality. For instance, metal hydroxide were structured on the surface of conventional zeolite to improve the interfacial adhesion,^{40,41} and mineral inorganics were uniformly coated on nanomaterials, serving as a space layer to interact better with polymer matrix.^{42,43} In recent researches, Zhang and co-workers innovatively developed a high-performance catalytic composite membrane through introducing Fe₃O₄@SiO₂ NPs into PES polymer matrix.⁴⁴ They coated the Fe₃O₄ NPs with SiO₂ via the hydrolysis of tetraethyl orthosilicate (TEOS). In the core-shell structure of Fe₃O₄@SiO₂ NPs, the Fe₃O₄ core could serve as a Fenton-like reaction catalyst while the SiO₂ shell is a hydrophilic surface layer (Fig. 3a). On account of this hydrophilic modification, the aggregation of Fe₃O₄ NPs was overcome, leading to effective dispersion in the polymer matrix. Moreover, the SiO₂ layer accelerated electrons migration in the catalytic

activity under mild conditions, and also improved the ability of radicals to catch organic pollutants. Aiming at the further inhibition of aggregation, 3-aminopropyltriethoxysilane, a silane coupling agent, was anchored on the silica surface via covalent bonds. After the modification, both permeability and porosity were improved, and the composite catalytic membrane showed high flux. Chung et al. decorated ZnO NPs onto GO nanosheets through a sol-gel process and then blended them in PSf membranes.⁴⁵ In this study, GO nanosheets acted as a platform to force the dispersion of ZnO NPs by pre-immobilization, and the ZnO-decorated GO could be well dispersed in the membrane matrix (Fig. 3b). The results show that the membrane properties are improved after the functionalization, including the permeability, humic acid rejection, antifouling, and antibacterial properties.

An alternative strategy is to use organic-inorganic composite nanofillers instead of inorganic ones to alleviate the incompatibility at the interfaces. Organic nanofillers that are compatible with the polymer matrix serve as a carrier to bring inorganic components into a composite membrane. For example, Ag NPs were immobilized on thermo-responsive poly(*N*-isopropylacrylamide) (PNIPAM) nanogel surfaces based on a polydopamine (PDA) coating, and then blended in PES casting solution to fabricate a catalytic membrane via vapor-induced phase separation (Fig. 3c).⁴⁶ The Ag-loaded nanogels were distributed on the membrane pore walls, and thereby membrane permeability could be adjusted by the temperature to achieve optimal catalytic performance. Such PNIPAM nanogels assembled at the pore/matrix interfaces show excellent stability during long-term operation because of their strong compatibility.

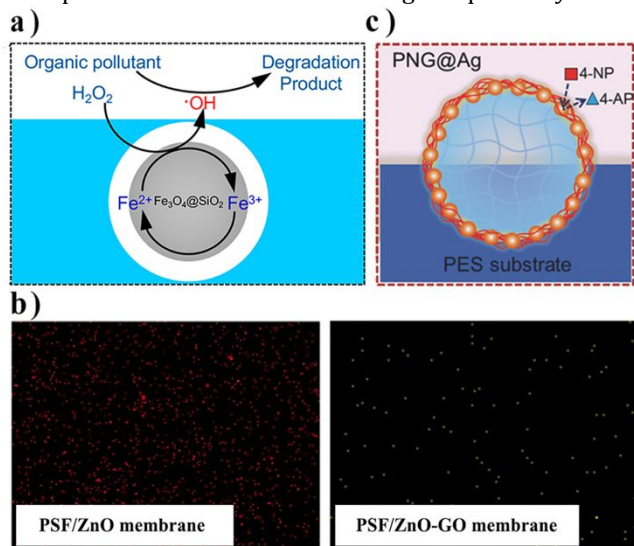


Fig. 3 a) Schematic illustration of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs in a membrane; b) FESEM mapping images of PSF/ZnO and PSF/ZnO-GO membrane and c) Schematic illustration of the Ag-loaded nanogel at the membrane/feed interface. Reproduced with permission from ref. 44, 45 and 46. Copyright 2019, 2017, Elsevier; Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA.

2.2 Pre-modification of polymers or addition of a third component

Pre-modification of polymers with functional groups, specific side chains, or blocks is another effective way to

promote interfacial compatibility between inorganic and organic components. Polar groups like sulfonic acid or carboxyl groups have been grafted to polymer matrices, not only for hydrophilization, but also providing active sites to capture inorganic components.^{47,48} For instance, sulfonated PSf was synthesized through facile electrophilic substitution and blended with TiO_2 to fabricate an organic-inorganic composite membrane for the removal of toxic Cr (VI) in wastewater.⁴⁹ The interfacial compatibility between PSf and TiO_2 was improved because of their hydrogen bonds.

Polymer side chains like PAA have also been grafted to polymer matrices. Zhang et al. developed a nanocomposite hollow fiber membrane based on PVDF grafted with PAA and TiO_2 through a sol-gel process.⁵⁰ The PAA was grafted onto PVDF via irradiation polymerization by a ^{60}Co γ -ray source. Due to the coordination interaction between Ti^{4+} and the carboxyl group of PAA, Ti^{4+} ions were enriched and formed TiO_2 NPs in situ within the matrix. The as-prepared membrane exhibited a uniform distribution of TiO_2 , leading to extremely prominent water flux and antifouling property.

Compared with the direct modification of polymer matrices, adding a third component into the matrix is more versatile and has been extensively used. The triblock copolymer PEO-PPO-PEO (Pluronic F12), which possesses segments that can interact with both the organic component and inorganic component, was introduced into the casting solution to enhance interfacial compatibility.⁵¹ Recently, Wang and co-workers added a third component, poly [hexafluorobutyl methacrylate]-poly [methacrylic acid]-poly [(2-(methacryloyloxy) ethyl) trimethyl ammonium chloride] (PHFBM-PMAA-PMTAC), as a multifunctional additive into a casting solution comprised of PVDF and AgNO_3 to construct a composite membrane integrating active and passive antifouling processes.⁵² Ag^+ ions were reduced by NaHB_4 to generate Ag NPs simultaneously during the non-solvent induced phase separation. The PHFBM segments were hydrophobic and compatible with the PVDF matrix due to the similar fluorinated chains, while the PMAA segments and the PMTAC segments were both hydrophilic to enhance membrane surface wettability. Carboxyl groups from the PMAA segments could coordinate with Ag NPs robustly. Consequently, Ag NPs were well dispersed on the surface and in the matrix because of the entanglement effects with the polymer chains (Fig. 4a). Moreover, some Ag NPs would spontaneously segregate to the membrane surface with the hydrophilic segments during the membrane formation. These hydrophilic chains on the surface could improve the membrane permeability and endow the membrane with good fouling resistance. The prepared membrane exhibited antibacterial properties and antifouling properties synergistically. Though effective, a challenge lies in design and synthesis of a specific new block copolymer for each distinctive nanocomposite membrane system. These syntheses may be complex and difficult to scale-up.

In addition to the block copolymer used above, manifold cross-linked agents are also used as the third component to fabricate a network with the aim of immobilizing nanofillers.

For example, Rajput et al. added styrene and divinyl benzene into poly (vinyl chloride) (PVC) solution and initiated their polymerization by azobisisobutyronitrile (AIBN) to form an interpenetrating network, and then utilized SGO as nanofillers to synthesize a cation exchange membrane for desalination via electrodialysis.⁵³ The interpenetrating network between PVC chains improved the thermal and mechanical stability of the membrane. In order to further enhance ion-exchange capacity and reduce the aggregation of SGO, they sulfonated the prepared membrane using chlorosulfonic acid. The SGO became more stable in the polymer matrix, and its dispersibility was greatly improved, which benefited from the hydrogen bonds formed between SGO and sulfonated styrene of the interpenetrating network (Fig. 4b). Some dispersants or compatibilizers like PVP were often added into the casting solution to reduce the aggregation of nanofillers.^{54,55} Except for the synthetic polymers, natural polymers such as polysaccharide normally have more polar groups which can serve as interacting sites. The nanofillers could be stabilized by adding a third component like polyethylene glycol,⁵⁶ cationic polymer⁵⁷ or sulfonated chitosan⁵⁸ that will form interactions with both nanofillers and polymers.

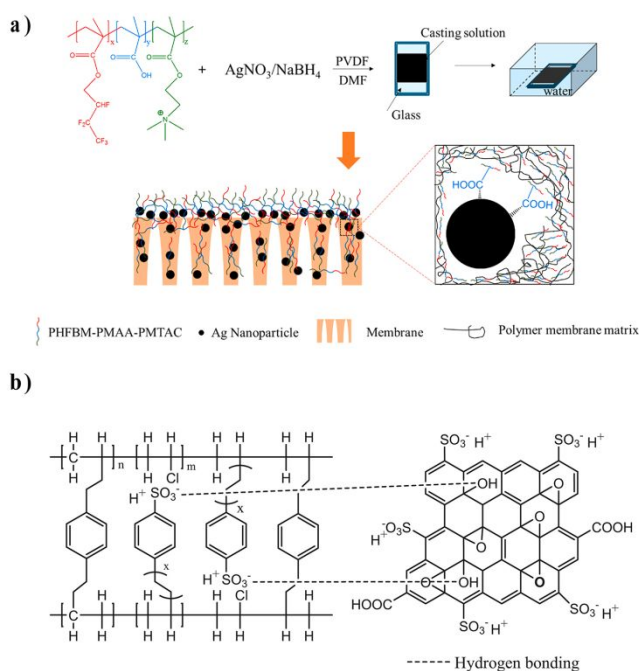


Fig. 4 a) Fabrication process and structure of a PVDF/Ag/PHFBM-PMAA-PMTAC membrane. b) Schematic illustration of the interactions within an interpenetrating network/SGO composite membrane. Reproduced with permission from ref. 52 and 53. Copyright 2019, 2018, Elsevier.

3. Molecular interfacial engineering in interface composite membranes

Compositing inorganic components onto as-formed membranes is another approach toward organic-inorganic composite membranes, and we first proposed the concept of “interfacial composite membrane” in 2016,⁵⁹ which refers to

a composite membrane with inorganics located on the membrane surfaces (including the pore walls). Compared with blending inorganic components in casting solution, this method can achieve a higher inorganic surface coverage. The biggest challenge to integrate inorganic nanomaterials with the polymer membranes lies in the poor interfacial compatibility between organic and inorganic components, and molecular engineering of the organic-inorganic interface provides an effective way to address this issue.

In this section, we summarize two mainstream protocols, “anchor-to” and “grow-from,” which enhance the organic-inorganic interface in composite membranes and present the most recent advances in this filed.

3.1 “Anchor-to” strategies

The “anchor-to” strategy is to engineer the polymer surface and/or inorganic particle surface with “donor” and “receptor” moieties, creating a strong and specific linkage at the organic-inorganic interface. The specific interactions include electrostatic interactions, hydrogen bonds, coordination, or even covalent bonding.

In some early studies, sulfonic acid groups were introduced onto commercial PES membranes as anchoring sites to capture TiO_2 NPs.^{60,61} Then Elimelech’s group presented a series of interface composite membranes based on “anchor-to” strategies. They modified PSf ultrafiltration membranes with reactive and/or charged functional moieties via oxygen plasma activation and incubated the obtained membrane in a solution containing PEI-grafted Ag NPs.⁶² Robust electrostatic and covalent bonds formed between the amines from PEI and the carboxyl moieties on the membrane surface after plasma treatment. In another example, using PVDF ultrafiltration membranes, the same group grafted negatively charged PMAA chains onto the PVDF membrane surface via plasma-induced grafting polymerization, and similarly immersed the plasma treated membrane into the amino-grafted SiO_2 NPs solution.⁶³ Carboxyl moieties on PMAA acted as the binding sites to attract amino-grafted SiO_2 NPs. These examples required pre-modification or pre-treatment of both membrane surfaces and inorganic nanomaterials. Elimelech et al. also demonstrated a facile and scalable approach to anchor bare SiO_2 NPs onto an alkaline-treated PVDF membrane surface grafted by (3-aminopropyl) triethoxysilane.⁶⁴ In the later research, the hydroxylated PVDF membrane surface was grafted with trimesoyl chloride, which reacted with Si-OH groups to anchor Ag/ SiO_2 nanocomposites for antifouling and antibacterial properties.⁶⁵ Functional complexes like polyoxometalate could be also immobilized onto the membranes through the “anchor-to” strategy (Fig. 5a).⁶⁶

Recently, the “anchor-to” strategy was employed in developing organic-inorganic thin-film composite (TFC) membranes. For instance, GO-Ag NPs composites, with well-known anti-microorganism activity, were covalently connected onto a polyamide top layer via amide bonds.⁶⁷ Both nanocomposite and polyamide surfaces were pre-modified with carboxyl groups. After grafting ethylene

diamine on TFC membranes through EDC/NHS mediation, the EDC/NHS activated GO-Ag composites were then linked onto the membrane surface (Fig. 5b).

However, limits of the “anchor-to” strategy lie in the arduous process of engineering “donor” and “receptor” moieties and effects of the reaction sites density on the inorganic coverage. Moreover, the diffusion of NPs into the inner pores of membrane is difficult when the particle size is close to the pore size; in such cases, the inorganics are only composited on the top surface rather than the pore walls.

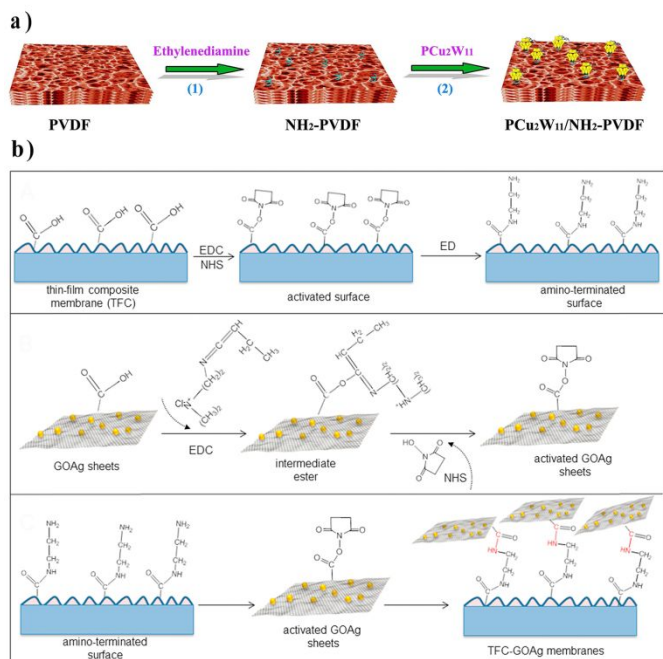


Fig. 5 Fabrication process of a) $\text{PCu}_2\text{W}_{11}/\text{NH}_2\text{-PVDF}$ interface composite membrane and b) binding GO-Ag nanosheets on the TFC membrane. Reproduced with permission from ref. 66 and 67. Copyright 2017, Elsevier.

3.2 “Grow-from” strategies

In situ growth of inorganic components from the membrane surface provides a “bottom-up” strategy that can tailor the inorganic layer more easily. The growth of minerals can be realized at the liquid-solid interface (e.g. bio-inspired mineralization) or the gas-solid interface (e.g. atomic layer deposition).

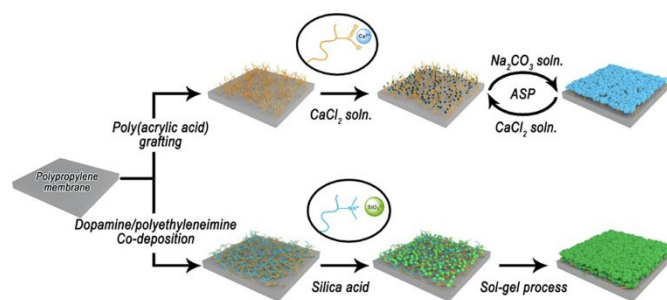


Fig. 6 Typical processes of bioinspired mineralization for interface composite membrane construction.

Xu’s group first proposed the bio-inspired mineralization strategy to fabricate organic-inorganic composite membranes.⁶⁸⁻⁷³ Inspired by bio-mineralization, an intermediate layer that can interact with mineral precursors is first constructed on the membrane to enrich the precursors and initiate mineralization. The first example was CaCO_3 -coated PP microfiltration membranes based on the interaction between Ca^{2+} and $-\text{COO}^-$ from PAA pre-grafted on the membrane (Fig. 6).⁶⁸ The PAA intermediate layer could not only provide binding sites for CaCO_3 growth but also stabilize the amorphous CaCO_3 to control the mineral layer thickness. Following that pioneering work, the same group developed a series of mineralized membranes based on a multifunctional mussel-inspired intermediate layer. The PDA/PEI layer⁷⁴ can provide the positive amino groups for silicification (Fig. 6),⁷¹ and catechol groups for chelating metal ions.⁷⁰ The rigid hydrophilic mineral coatings showed excellent anti-oil property in water, enabling these mineralized membranes to be used in oil-in-water emulsion separation. Such property is also desirable in Li-ion battery separators to improve electrolyte wetting and resist thermal shrinkage.⁷⁵

Since the original work by Xu’s group, PDA-based interlayers have been widely applied to construct organic-inorganic composite membranes. For example, Cui and co-workers grew nickel cobalt layered double hydroxide (NiCo-LDH) on a PDA-modified PVDF membrane via a facile and low-temperature hydrothermal method (Fig. 7a).⁷⁶ Catechol groups from the PDA layer could chelate Co^{2+} and Ni^{2+} ions, initiating the growth of a NiCo-LDH nanoarray. The tunable grass-like surface structure promoted hydrophilicity and underwater oleophobicity of the membrane, making it suitable for oil-water emulsion separation. The enhanced interface compatibility between NiCo-LDH and PVDF granted the composite membrane outstanding recycling performance.

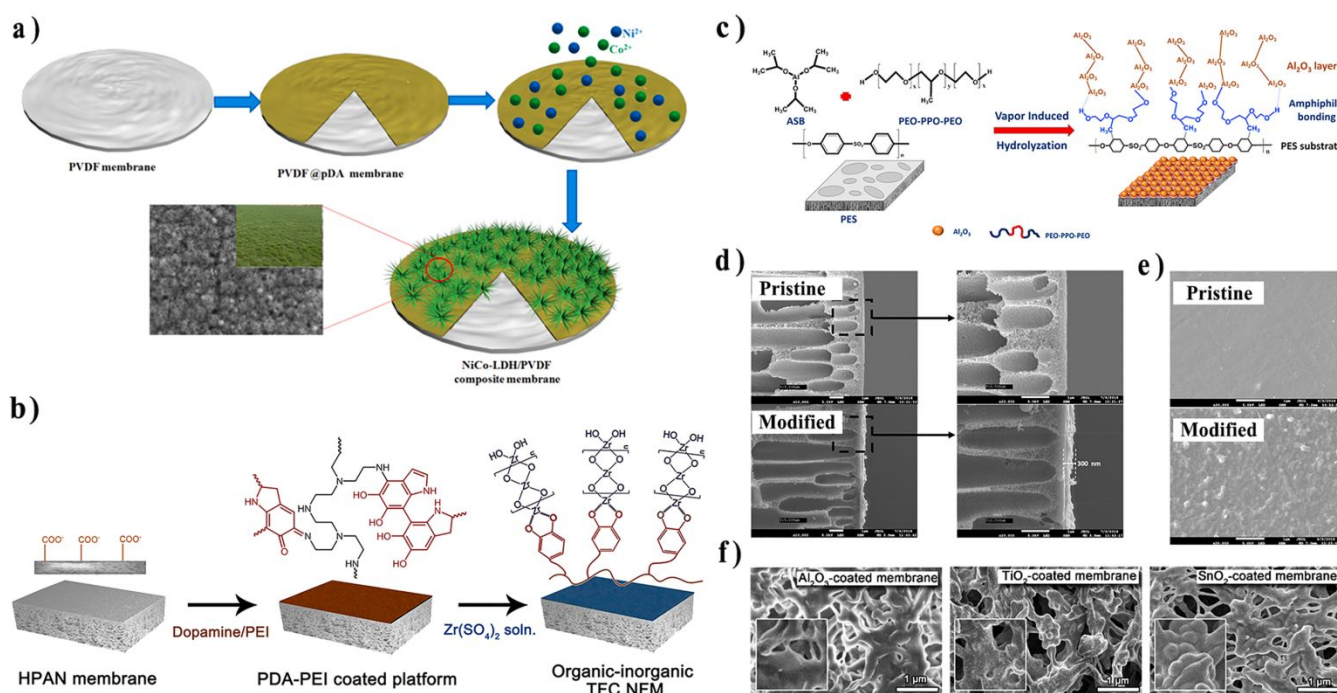


Fig. 7 Schematic illustration of the fabrication process of a) NiCo-LDH/PVDF interface composite membrane, b) ZrO₂/PAN TFC membrane, and c) Al₂O₃/PES composite hollow fiber membrane. d) Cross-sectional SEM images and e) SEM images of Al₂O₃/PES composite hollow fiber membrane surface. f) SEM images of PVDF membranes coated with Al₂O₃, TiO₂, and SnO₂ by ALD. Reproduced with permission from ref. 76, 77, 80 and 86. Copyright 2019, 2016, 2017, Elsevier; Copyright 2018, American Chemical Society.

Mineralization strategies have been also applied to fabricate organic-inorganic TFC membranes. For example, Lv et al. grew ZrO₂ on a PDA/PEI-deposited substrates to enhance structural stability during nanofiltration (Fig. 7b).⁷⁷ Another example presented by Ding et al. deposited positively charged chitosan on PDA-modified PSf substrates via electrostatic interaction, and then initiated the hydrolysis through the Stöber method.⁷⁸ Compared with the single intermediate PDA layer, the additional positively charged CS layer overcame the partial congregating of PDA and served as a smooth platform for uniform in situ growth of SiO₂, leading to a dense and defect-free inorganic layer.

The inorganic layer can also be further modified to realize even more sophisticated functionality. Wongchitphimon et al. modified Matrimid® membranes with trimethoxysilane to introduce amide groups on the membrane surface, and subsequently immersed the membrane into TEOS for silicification.⁷⁹ Consequently, the membrane was grafted with a fluorinated silane to achieve a non-wetting state, which displayed bright prospects in the recovery of methane dissolved in anaerobic effluent.

In addition, Lin and co-workers immersed PES hollow fiber membranes into a mixed solution composed of Al₂O₃ precursor, aluminum-tri-sec-butoxide (ASB), and a tri-block copolymer, PEO-PPO-PEO. A uniform and continuous Al₂O₃ layer could be easily achieved by in situ vapor-induced hydrolyzation (Fig. 7c-e).⁸⁰ The structure and performance of the membrane could be adjusted by the amount of ABS. In this research, the amphiphilic PEO-PPO-PEO played a vital

role in bridging the substrate and precursors. The PPO segments would be attracted by PES through hydrophobic interactions, while the PEO segments could capture the precursor by hydrogen bonds.^{81,82} PEO-PPO-PEO provided growth sites for Al₂O₃, improving the affinity of inorganics to the organic substrate, and addressed the issue of poor interface compatibility.

Atomic layer deposition (ALD) is another appealing technique to construct adaptable and uniform inorganic coatings on polymeric membranes.⁸³ In a typical ALD process, the reactive precursor vapors are pulsed into the chamber alternatively under the protection of inert gas, leading to the layer-by-layer growth of metals, metal oxides, and even organic materials.^{84,85} Our recent research demonstrated the deposition of a series of oxides, including ZnO, Al₂O₃, TiO₂, and SnO₂, on PVDF membranes (Fig. 7f). ALD provided the best strategy to construct various inorganic layers with controllable thickness, which could be used to investigate the anti-crude-oil properties of different oxides.⁸⁶ In our research, PVP added in the commercial membranes provided the nucleation sites for ALD eliminating the need for surface pre-treatment. However, for certain extremely inert substrate materials (e.g. PP or PTFE), ALD nucleation becomes difficult and particles instead of a uniform coating form. Both plasma and nitric acid activation have been proposed to facilitate ALD process in such scenarios.⁸⁷⁻⁸⁹ In addition, the ALD layer can also serve as an intermediate layer for further modification.^{90,91} More examples could be found in our recent review.⁸³

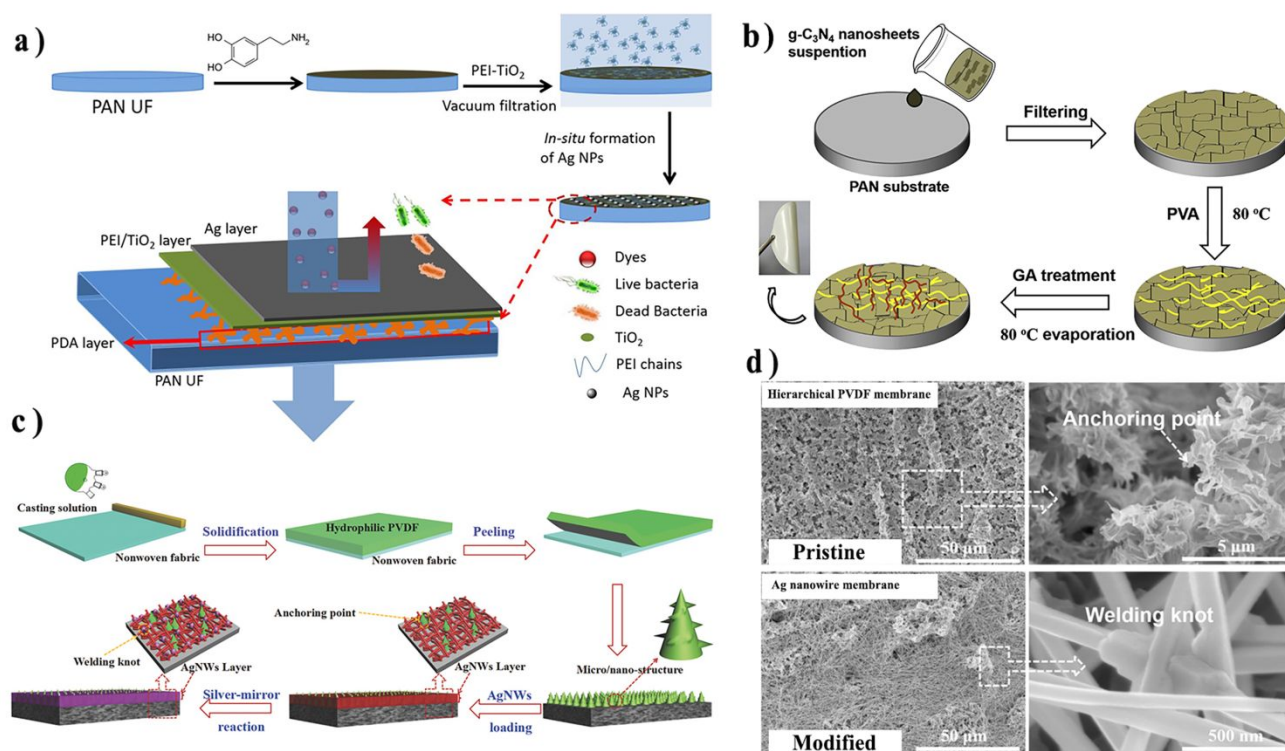


Fig. 8 Fabrication process of a) PEI-TiO₂/Ag composite PAN membrane, b) g-C₃N₄ nanosheets dual-layer composite membrane, and c) Ag nanowire dual-layer composite membrane. d) SEM images of pristine hierarchical PVDF membrane and Ag nanowire membrane surfaces after silver-mirror reaction. Reproduced with permission from ref. 92, 96 and 93. Copyright 2019, Elsevier; Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA.

4. Molecular interfacial engineering in dual-layer composite membranes

Distinct from interface composite membranes, there is another kind of composite membrane with a macroscopic inorganic layer and a polymer layer, which is typically fabricated by vacuum filtration of inorganic nanomaterial suspension through a polymer membrane. The inorganic materials are rejected by the membrane pores and form a filtration cake layer on the membrane surface. These composited membranes are named “dual-layer composite membrane” in this review. In such membranes, the polymer substrate serves as a support layer, while the inorganic layer plays a crucial role in separation or other functions. The inorganic nanomaterials could be NPs⁹², nanowires⁹³, nanotubes⁹⁴, or nanosheets⁹⁵. As with other composite membranes, stability between the two layers is a persistent challenge, especially under cross-flow operation. Therefore, some interface molecular engineering has been conducted to enhance the interface strength, and herein we provide several examples to present the recent advances in this field.

Pre-modification of the support and/or inorganic layers is another approach for promoting interfacial compatibility. For example, Li et al. modified TiO₂ NPs with PEI and deposited the modified NPs onto the surface of PDA-coated PAN ultrafiltration membranes via vacuum filtration.⁹² PDA could interact and even react with PEI to stabilize the particle layer on the membrane surface. Ag NPs layers were further synthesized on the particle layers to endow the membranes

with anti-bacterial activity (Fig. 8a). In these membranes, the PDA layer served as the adhesive layer to connect substrate and TiO₂ NPs, the PEI-TiO₂ layer acted as the separation layer, and the Ag NP layer provided the antibacterial function.

Another strategy is to add a third component to connect/enclose inorganic nanomaterials with the support layer. Li et al. filtrated graphitic carbon nitride (g-C₃N₄) nanosheets on PAN substrate surfaces and then stabilized the nanosheet layer by constructing a cross-linked network by polyvinyl alcohol and glutaric dialdehyde, which prevented the detachment or damage of nanosheets (Fig. 8b).⁹⁶

Combining the above strategies, Xiong and co-workers developed a robust multi-functional composite membrane by weaving the adjacent interconnected Ag nanowire (Ag NWs) network on the PVDF membrane surface inspired by Chinese knots (Fig. 8c).⁹³ The PVDF substrate was pre-designed with a micro/nano hierarchical surface during the phase-inversion process. Compared with the smooth membrane surface, structured surfaces could provide more anchoring points for attaching the Ag NWs.^{97,98} After filtration of Ag NWs onto the membrane surface, the silver mirror reaction was conducted to integrate the deposited Ag NWs and tighten the connection between Ag NW layer and membrane (Fig. 8d).

Conclusions and perspective

Benefiting from the enhanced performance and special functions granted by inorganic components, organic-

inorganic membranes have attracted burgeoning attention in water technology. Since organic-inorganic interfaces are vital for these membranes, tremendous effort has been devoted to improving the interface compatibility through molecular engineering strategies. In this review, we summarized the molecular engineering strategies toward interface control in three classes of organic-inorganic composite membranes. In mixed matrix membranes, molecular engineering is generally completed before the membrane formation. The inorganic fillers or/and polymer matrix were pre-modified by small molecules or polymer chains to achieve a more compatible interface during the phase-separation process. A third component could also serve as an amphiphilic link to stabilize the incompatible interface. In interface composite membranes, the “anchor-to” and “grow-from” strategies were proposed to construct an inorganic layer on the surface of a polymer skeleton. The former engineers the as-prepared nanomaterials and/or polymer surface to realize a “donor-receptor” interaction. In contrast, the latter tries to in situ grow the mineral layer at a liquid-solid or gas-solid interface, which is more controllable in thickness and inorganic coverage. In dual-layer composite membranes, the interfacial engineering is most likely to provide a robust connection between the organic and inorganic layers for enhanced stability in a cross-flow cell. Both covalent/non-covalent interactions and interlocking structures can achieve this goal by molecular or structural design.

Despite these recent advances in organic-inorganic membranes, there are still some challenges lying on the road to the industrial production of these membranes. Firstly, high inorganic coverage and significant performance improvement could be easily achieved by some interface composite strategies (e.g. ALD and bio-inspired mineralization). However, the sometimes high fabrication cost, complicated process, or expensive facilities limit their practical applications at the large scales necessary for real-world water treatment. More economical and scalable techniques are highly desirable. Secondly, even for the mixed matrix membranes, large-scale engineering of inorganic nanomaterials remains challenging and uneconomic. Thirdly, most of the dual-layer composite membranes are fabricated by vacuum filtration, which can be only conducted at the laboratory scale. From a foundational perspective, how the interfacial interactions affect the membrane formation at the micro-scale is still unclear, which is critical for understanding the structure-performance relationships and ultimately designing optimized organic-inorganic composite membranes. Except for addressing the above-mentioned challenges, the future research opportunities also lie in developing novel membranes. For example, Janus membrane is an emerging concept of a membrane with opposing properties on each side, which can find widespread applications in multiphase-phase processes.^{99,100} An organic-inorganic Janus membrane was developed to fast separate trace blood for glucose measurement.¹⁰¹ The inorganics can bring fantastic properties to the Janus membrane.

Conflicts of interest

There are no conflicts to declare.

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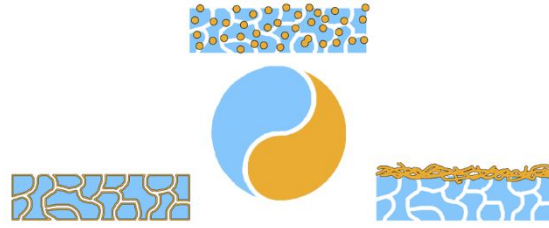
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Molecular Engineering of Organic-Inorganic Interface

Recent progresses on molecular engineering in organic-inorganic composite membranes are presented.