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Preparation of Hydrophobic Membranes and Their Applications in Various Areas

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Abstract. Hydrophobic membranes are increasingly being recognized for their versatile applications across a wide range of fields, including corrosion protection and separation processes. Their ability to repel water and resist fouling makes them highly valuable for enhancing the durability and extending the service life of various industrial, consumer products and so on. This paper conducts a comprehensive review of the preparation methods for different types of hydrophobic membranes, based on an analysis of relevant existing literature. The study places particular emphasis on current societal and industrial priorities, exploring how these membranes are utilized in key areas such as corrosion resistance, chemical separation, and marine engineering. Furthermore, it delves into the fundamental mechanisms that underpin their hydrophobic properties. This review reveals that significant advancements have been made in the development of diverse fabrication techniques for hydrophobic membranes. Notably, there is a growing trend toward more environmentally friendly and sustainable preparation methods, aligning with global green chemistry initiatives. Moreover, the application of hydrophobic membranes is expanding beyond heavy industry into everyday products and scenarios, indicating their growing integration into daily life and their potential to contribute to more durable, efficient, and sustainable technologies in the future.

Keywords: Hydrophobic membrane, Corrosion resistance, Separation

1. Introduction

This review systematically examines the preparation methods and diverse applications of hydrophobic membranes by synthesizing findings from existing literature. Hydrophobic membranes are a specialized class of functional materials characterized by their ability to repel water molecules. Their hydrophobic performance is typically quantified using the water contact angle: a contact angle greater than 90° indicates hydrophobicity, while an angle exceeding 150° corresponds to superhydrophobicity. These distinctive properties mainly originate from the membranes' micro-/nanoscale surface roughness and low surface energy chemical composition, which together enable broad and promising applications across various fields. Furthermore, numerous fabrication methods have been developed to produce such membranes, extending their practical utility across a wide range of domains.

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In practical terms, hydrophobic membranes play a crucial role in enhancing the corrosion resistance and operational lifespan of industrial equipment, enabling efficient and low-energy oil-water separation, and advancing seawater desalination and resource recovery technologies—thereby addressing pressing real-world challenges such as environmental pollution and resource scarcity. From an industrial perspective, the preparation pathways and application cases summarized in this paper provide valuable references for the research, development, and selection of related engineering materials, promoting their adoption and implementation in sectors such as energy, chemicals, and marine engineering. Academically, this study offers a systematic overview of the current progress and remaining challenges in hydrophobic membrane preparation and application. It also provides a comprehensive knowledge base and directional guidance for future research in this field.

2. Preparation of hydrophobic membranes

2.1. Preparation of hydrophobic membranes based on the biomimicry from nature

Most of organism possesses unique surface structures and the knowledge of biomimicry supplies some creativity to the preparation of high-performance hydrophobic membranes. In this paper, rice leaves are taken as the biomimetic prototype, and polyvinylidene fluoride (PVDF) superhydrophobic membranes with anisotropic characteristics are successfully constructed using electrospinning technology. The unique micro-nano structure and directional arrangement of the rice leaf surface enable it to exhibit an extremely low rolling angle in the direction parallel to the leaf veins, guiding the directional movement of water droplets. Through systematic optimization of the spinning solution ratio and process parameters, a nanofiber membrane with highly aligned fibers and a biomimetic micro-nano structure on the surface is prepared under the conditions of a DMF and acetone solvent ratio of 5:5, a PVDF mass fraction of 22%, a voltage of 12 kV, a push rate of 0.05 mm/min, and a roller speed of 2200 r/min. This membrane exhibits excellent superhydrophobic performance, with a water contact angle reaching up to 149.5°. This research not only proves the effectiveness of biomimicry in functional material design but also creates a new technological path for the development of advanced membrane materials with potential applications such as directional liquid transport, self-cleaning, and efficient oil-water separation [1].

2.2. Preparation of hydrophobic membranes using SiO_2 as one of the raw materials

Xu Jiaqi and others prepared a core–shell SiO_2 sol with fluorine-containing modifiers as the core via the sol–gel method, and compounded it with silicone-modified polyurethane resin. By employing the breath figure technique, they in situ constructed a porous composite membrane with a lotus-inspired micro–nano structure on a glass surface. This composite membrane exhibited excellent superhydrophobicity, achieving a water contact angle of up to 153.1°, as shown in Figure 1. It also demonstrated remarkable self-cleaning ability, with a low stain retention rate of approximately 4% [2].

Studies showed that the core–shell SiO_2 sol, with a particle size matching that of the polymer, not only enhanced the mechanical stability and adhesion of the coating (reaching grade 1) but also addressed the poor durability typically associated with pure polymer membranes. Furthermore, by adjusting the film-forming process, the pore size of the porous structure was controlled to around 700 nm, which is smaller than the wavelength of visible light. This ensured superhydrophobicity while maintaining an average light transmittance as high as 91.5% [2].

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The resulting membrane exhibits good stability and long-term storage performance, meeting the daily optical transparency requirements of glass applications. This work provides an effective composite strategy and a practical fabrication pathway for developing transparent, highly hydrophobic, and mechanically durable self-cleaning coatings [2].

Figure 1. The water contact angle [2]

Furthermore, Peng Qianqian et al. synthesized alkylated SiO_2 nanoparticles via the sol-gel method and deposited them onto a polytetrafluoroethylene (PTFE) membrane by vacuum filtration, thus fabricating a SiO_2/PTFE composite membrane — referred to as the SP membrane — featuring a micro-nano rough structure, where SiO_2 serves as a key functional component [3].

The SP membrane demonstrates excellent superhydrophobicity, with a water contact angle up to 154°, while allowing oil droplets to penetrate rapidly within just one second. In oil-water separation applications, it exhibits high separation efficiency for various oil-water mixtures and water-in-oil emulsions (exceeding 97%), along with high permeation flux and stable performance over 10 reuse cycles. This method is facile, environmentally friendly, and provides a reliable pathway for developing high-performance oil-water separation membranes [3].

2.3. Preparation of superhydrophobic membrane on TC4

Wang Ying and others successfully fabricated a superhydrophobic composite film featuring a dual-scale micro-nano rough structure and low surface energy, with the preparation process illustrated in Figure 2.

This superhydrophobic film was developed by employing micro-arc oxidation technology to in situ grow a ceramic layer—composed mainly of anatase and rutile TiO_2 along with amorphous SiO_2—on the titanium alloy surface, thereby forming a multilevel rough structure interwoven with micron-scale protrusions and nano-scale pores. Subsequently, surface modification was carried out using octadecyltrimethoxysilane, which not only effectively filled the micropores and cracks in the micro-arc oxidation layer but also significantly lowered its surface energy.

The resulting Ti-MAOOTMS superhydrophobic composite film exhibited a water contact angle of 154.0° ± 1.8° and a rolling angle of about 3°, demonstrating pronounced superhydrophobicity. Electrochemical tests revealed that the superhydrophobic coating reduced the corrosion current density by nearly four orders of magnitude, shifted the self-corrosion potential positively by 0.934 V, and increased the impedance by two orders of magnitude. Moreover, it maintained excellent corrosion resistance and hydrophobic stability after one-week immersion in 3.5 wt% NaCl solution.

By trapping air to form a gas-layer barrier, this composite film effectively prevents corrosive media from contacting the substrate, offering a promising strategy for the long-term protection of titanium alloys in highly corrosive environments such as marine settings [4].

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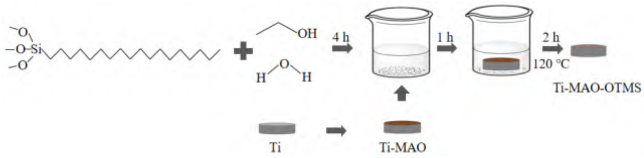

Figure 2. The preparation process of the Ti-MAO-OTMS [4]

3. The application of hydrophobic membranes

3.1. Corrosion resistance field

This research focuses on the development and characterization of a novel superhydrophobic composite membrane based on a copper-metal organic framework modified with sodium alginate (Cu-MOF-SA) and its functional application in corrosion protection for AZ31 magnesium alloy substrates. Magnesium alloys, despite their favorable strength-to-weight ratio, face significant limitations in engineering applications due to their high susceptibility to corrosion. To address this challenge, a micro-nano hierarchical structured Cu-MOF-SA superhydrophobic coating was successfully fabricated on the alloy surface through a straightforward and efficient one-step electrodeposition process. The synthesized surface exhibits exceptional water repellency, achieving a static water contact angle of up to 158°, which clearly demonstrates its pronounced superhydrophobic characteristics [5].

The fabricated superhydrophobic coating functions as an effective physical barrier that significantly impedes direct contact between the underlying magnesium alloy substrate and aggressive corrosive media. Electrochemical corrosion evaluations conducted in a 3.5 wt.% NaCl solution reveals substantially enhanced corrosion resistance. Notably, the coating induces a positive shift in corrosion potential by approximately 0.24 V, reduces the corrosion current density by more than one order of magnitude, and considerably increases the polarization resistance compared to the uncoated alloy. Furthermore, the study systematically evaluates the environmental stability of the coating. It demonstrates remarkable chemical stability across a wide pH spectrum, maintaining its superhydrophobic property after 24-hour immersion in aqueous solutions with pH values ranging from strongly acidic (pH 1) to strongly alkaline (pH 14). The coating also exhibits excellent thermal stability, as it retains a water contact angle above 154° following exposure to air at temperatures varying from 20°C to 90°C, while continuing to provide consistent and effective corrosion protection under these conditions [5].

3.2. Chemical separation field

Given the frequent occurrence of industrial oily wastewater and offshore oil spill incidents, the development of efficient and low-cost oil–water separation technologies has become an urgent priority. In this context, superhydrophobic membranes have garnered extensive research interest owing to their high separation efficiency, low energy consumption, operational simplicity, and excellent selectivity [6].

Superhydrophobic membranes achieve highly efficient separation of oil–water mixtures through precise engineering of surface wettability. They exhibit particularly outstanding performance in treating both floating oils and stable emulsified oils. Numerous fabrication methods have been explored and reported, including dip-coating, electrospinning, plasma-enhanced chemical vapor deposition (PECVD), and sol–gel processing. These membranes can be constructed from a wide range of substrates, such as stainless steel meshes, polymer films, ceramic supports, and nanofiber

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assemblies. For example, graphene-based composite membranes, polylactic acid (PLA) porous membranes, and polyvinylidene fluoride (PVDF) nanofiber membranes have all demonstrated not only high separation efficiency but also remarkable durability and reusability in continuous operation [6].

3.3. Marine field

The main technique of hydrophobic membranes in the marine field, which is seen as one of the most significant methods to deal with the problem of global water scarcity, especially by utilizing the vast seawater resources. The membrane distillation process utilizes porous hydrophobic membranes as key materials, and its working principle is to use hot seawater, such as the feed liquid, which flows on one side of the membrane, causing water molecules to vaporize upon heating. The generated water vapor is driven by the vapor pressure difference on both sides of the membrane and passes through the micropores of the membrane. On the other side of the membrane, the cold end, water vapor is condensed to obtain high-purity fresh water, while salt and other non-volatile solutes in seawater are effectively intercepted by the hydrophobic membrane [7].

Compared with the traditional reverse osmosis technology, membrane distillation technology based on hydrophobic membranes has significant advantages: first of all, it can handle higher concentrations of saltwater, which has a freshwater recovery rate of over 80% and a salt retention rate of over 99%. What's more, the high concentration effluent produced does not need to be directly discharged back into the sea and can be used as a chemical raw material to achieve "zero emissions", which play a vital role in protecting sensitive marine ecosystems. The paper introduces four main membrane distillation configurations (which are DCMD, AGMD, SGMD and VMD), all of which rely on hydrophobic membranes to achieve gas-liquid separation [7].

However, the complex chemical environment of natural seawater, such as high salinity, organic matter, and microorganisms, has caused a serious challenge to the long-term stability of membrane materials. The early use of organic polymer hydrophobic membranes (such as PTFE and PVDF) was prone to swelling and contamination, which limited their industrial application. Therefore, research has shifted towards inorganic ceramic films with excellent chemical stability, mechanical strength, and corrosion resistance. But ceramic membranes have hydrophilicity and must be modified with hydrophobicity before they can be used for membrane distillation [7].

Finally, the highly stable all-inorganic ceramic hydrophobic membrane obtained through polymer pyrolysis modification has shown great potential for application in membrane distillation seawater desalination. Its excellent durability and anti pollution ability make it a core key material for achieving efficient, sustainable, and environmentally friendly "zero emission" marine freshwater acquisition technology [7].

4. Conclusion

This article mainly discusses the preparation of different hydrophobic membranes and focuses on analyzing their applications in the corrosion resistance field, chemical separation field and marine field. Hydrophobic membranes play a crucial role in effectively blocking corrosive media or achieving selective separation of oil and water through their surface properties. This paper has a shortage on an interdisciplinary perspective, such as not combining machine learning algorithms to screen the optimal preparation parameters or drawing on surface acoustic wave technology to develop a real-time monitoring scheme for membrane fouling, which always limits the development of intelligent response capabilities for complex working conditions. In the future, research and development have a great chance to focus on studying hydrophobic membranes with self-healing capabilities, which can enable the membranes to automatically repair their membrane structure and extend their service life after damage.

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