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# Recent progresses on fabrication of photocatalytic membranes for water treatment

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ABSTRACT

Compared to conventional separation membranes, photocatalytic membranes possess a number of unique properties, such as anti-fouling, anti-microbial, superhydrophilicity, concurrent photocatalytic oxidation and separation, all of which make them an attractive technology in water treatment. Moreover, the problem of photocatalyst separation which is the main obstacle of photocatalysis processes can be resolved by the photocatalytic membranes thereby advancing their practical application. This article presents an overview of this new type of membrane, with a focus on recent progresses achieved on their fabrication methods. Based on membrane materials, they are broadly categorized into pure inorganic and inorganic–polymer hybrid membranes. The fabrication methods are separately reviewed and discussed for these two membrane categories. In addition, future perspectives on membrane development and feasibility are given. The paper would provide new insights into the development of photocatalytic membranes and their potential in water treatment.

## 1. Introduction

In the last decades, membrane technology has been widely applied in water industry due to its small size, easy maintenance, excellent separation efficiency and high water quality [1]. However it still has some drawbacks which limit its practical application to some extent: (a) membrane fouling; (b) narrow operational boundary; (c) lack of ability to degrade pollutants. Hence, additional post-treatment processes are needed to treat membrane concentrates and the wastewater generated during membrane chemical cleaning. In recent years, photocatalytic membranes have attracted enormous interests in the industry and academia due to their highly desirable multi-modal functionalities and innovative designs which can potentially overcome these drawbacks associated with conventional membranes [2].

Photocatalytic oxidation has been intensive studied since the discovery of electrochemical photolysis of water by Fujishima and Honda in 1972 [3]. In theory, the photogenerated reactive oxygen species (hydroxyl radicals, superoxides) can completely degrade most of organic pollutants, bacteria and viruses. However, it is very difficult to reclaim photocatalysts from the treated water since their physical sizes are generally in nano range. Although some separation methods have been reported using membrane filtration [4], magnetic separation [5], these methods are energy-intensive and uneconomical. Another advantage of photocatalytic membranes is that there is no need for photocatalyst separation, which will advance the practical application of photocatalytic oxidation in water treatment.

Among a large volume of semiconductors available, $TiO_2$ is the most used photocatalyst due to its chemical and thermal resistance, low-cost and nontoxicity. Hence, most of photocatalytic membranes are made of $TiO_2$ based materials. The first $TiO_2$ membrane was fabricated by Anderson and co-workers in 1988 [6]. However, their study focused on membrane morphology and did not evaluate its photocatalytic activity. The term of "photocatalytic membrane" first appeared in their another paper published in 1991 [7]. The so-called "photocatalytic membrane" is actually a film on solid glass substrate rather than a "true" separating membrane. The separation function of photocatalytic membranes had not been studied until 2006 when Dionysiou's and Quan's groups reported $TiO_2/Al_2O_3$ [8] and $TiO_2/SiO_2$ [9] membranes, respectively. Both the permeability and photocatalytic activity of these membranes were evaluated. Inspired by their pioneering works, a large number of photocatalytic membranes have been fabricated via various synthesis methods, e.g. hydrothermal synthesis [2], anodization [10], liquid phase deposition [11], electrospinning [12] etc. Although about 20–40 journal papers are published each year and great progresses have been made in the past few years, there is still lacking of a comprehensive review to summarize these processes and provide critical perspectives for the future development.

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The major objective of this article is to summarize and discuss the fabrication methods of recently reported photocatalytic membranes. The main text is organized into two sections based on membrane materials, inorganic membranes and inorganic–polymer hybrid membranes. Finally, a personal perspective on the future of photocatalytic membranes is given. To avoid ambiguity, in this review, photocatalytic membrane is defined as "a permeable free-standing or supported layer on porous substrates that possesses photocatalytic activity under UV or visible light irradiation". Although the photocatalytic film in numerous papers was coined using "photocatalytic membrane" by the authors, these studies without demonstrable separation and permeability are not included in this review.

## 2. Inorganic photocatalytic membranes

### 2.1. Sol–gel method

Sol–gel method is a well-studied technique in the fabrication of $TiO_2$ photocatalytic membranes due to its versatility [13]. The sol–gel process starts with the hydrolysis of $TiO_2$ precursors (e.g. metal alkoxides) forming a sol. The $TiO_2$ sol is then coated onto a porous support via dip coating or spin coating. A supported $TiO_2$ membrane is obtained after calcination to achieve the crystalline transformation from amorphous to anatase or rutile phase.

The quality of the $TiO_2$ sol has significant impact on the properties of the final $TiO_2$ photocatalytic membrane. In order to obtain uniform $TiO_2$ sol, water is partially or completely replaced by acetic acid (AcOH) to slow down the hydrolysis rate [14,15]. Another approach is to lower the hydrolysis temperature using ice bath [9]. In contrast, Alem and co-workers [16,17] reported a new method. $TiO_2$ precursors were first added into excess water to achieve rapid hydrolysis and then the precipitate was washed and re-dispersed in water. Finally, the mixture was stabilized by $HNO_3$ to create a stable sol. The size of the sol particles prepared via this method is larger than that of conventional methods, being of 55.6 nm, which leads to a large membrane pore size. In addition, three coating layers are generally required to fabricate a $TiO_2$ skin layer with good structural integrity and without significant cracks and pinholes [8].

The pore size and porosity of the photocatalytic membranes can also be tunable via adding pore-directing agents into $TiO_2$ sol. For example, poly(oxyethylenesorbitan monooleate) (Tween 80) was applied by Choi and co-workers [8,14,18]. The resulting $TiO_2$ membranes exhibited high surface area and porosity, narrow pore size distribution, good homogeneity. Fig. 1 shows that the $TiO_2$ layer prepared using the $TiO_2$ sols with different molar ratios of Tween 80/titanium tetraisopropoxide = $R$:1 has a pore diameter of 2–6, 3–8 and 5–11 nm with increasing the $R$ from 1 to 3 [8]. Several other additives, such as chitosan [19], PEO [20] and PVA [16], have also been investigated. Moreover, the pH value of $TiO_2$ sol has a big impact on the microstructure and morphology of the resultant gel. Gel films are generally obtained in acid conditions due to gelation is inhibited in basic conditions. Recent study showed that the inhibition of gelation can be overcome by the addition of surfactants with hydrophilic poly(ethylene oxide) (PEO) blocks [21].

It is worth noting that thin $TiO_2$ layers were observed not only on the top of substrates, but also inside their pores [15]. It might compromise the permeability of the membranes since the pores are blocked due to sol infiltration. To avoid this, the substrates can be pre-coated with a polymer layer prior to $TiO_2$ coating. The polymer layer prevents $TiO_2$ sol entering inside of the pores during the coating process and is removed by pyrolysis during the calcination process. Nevertheless, if the pore size of a substrate is large enough, $TiO_2$ sol can form a tubular structure inside the substrate pores. This phenomena was utilized by Zhang and co-workers to fabricate $SiO_2/TiO_2$ nanotube composite membrane [9]. In addition, the $TiO_2$ layer can be restructured into other morphologies, such as needle-shape $TiO_2$ via alkaline post-treatment [22].

Besides the simplicity and ease of preparation, sol–gel processing is also a facile method for improving the photocatalytic activity of the $TiO_2$ membranes. One approach is to combine $TiO_2$ with other materials with a higher adsorption capacity, such as $SiO_2$ [9,23] and hydroxyapatite (HAP) [24]. These materials accelerate the accumulation of target pollutants on the surface of photocatalytic membrane, which in turn results in an improvement in photocatalytic oxidation rate [9]. The other strategy is to dope metals or non-metals into $TiO_2$ matrix [21], which can be achieved via simply mixing their inorganic salts into $TiO_2$ sol. The most commonly used metal is silver due to its ability of inhibiting recombination of electron–hole pairs and anti-microbial ability [24–26].

### 2.2. Liquid phase deposition method

Liquid phase deposition was first extended to fabrication of $TiO_2$ nanotube membrane using $TiF_4$ as precursor by Zhang and co-workers in 2008 [11]. After the addition of ammonia into $TiF_4$ solution, $TiO_2$ is produced by a stepwise reaction (Eq. (1)) via the hydrolysis of $TiF_4$.

$$TiF_4 \rightarrow Ti(OH)_4 \rightarrow TiO_2 \qquad (1)$$

Thin $TiO_2$ films are grafted through the heterogeneous nucleation on the surface of alumina substrate and inside its channels. A nanotube membrane is obtained after removing the $TiO_2$ film from the alumina membrane surface. With increasing grafting time, the wall of $TiO_2$ nanotubes became thicker resulting in a reduction of the inner diameter of these nanotubes. Although the alumina substrate can be removed by immersing the membrane in an ammonia solution, the physical strength of the unsupported membrane was observed to be very weak.

Wang and co-workers [27] reported a nitrogen doped $TiO_2$ nanotube membrane which was formed by using $(NH_4)_2TiF_6$ and urea. During the liquid phase deposition, urea was decomposed into ammonia, which resulted in nitrogen doping within the $TiO_2$ lattice. They also found that a substrate with small pore size could lead to a formation of $TiO_2$ nanorods rather than nanotubes.

Most recently, Pan and co-workers [28] proved that this method can also been applied for fabrication of mesoporous ZnO membrane using zinc nitrate and urea assisted by surfactants. $Zn_4(OH)_6CO_3 \cdot H_2O$ (ZCHH) microspheres which comprised of radially oriented nanoflake shells were first grafted on the surface of substrate via deposition-growth process. Upon calcination, ZCHH readily decomposes to nanocrystalline wurtzite-phase ZnO without significant change in the morphology, and the release of $CO_2$ and $H_2O$ creates an additional mesoporous structure in both hemispherical interior and nanoflake shell. The mesoporous membrane exhibits excellent performances in photocatalytic oxidation and membrane filtration.

### 2.3. Hydrothermal synthesis

Hydrothermal method has been intensively studied for the fabrication of $TiO_2$ nanowires. Under high pressure and temperature, the Ti—O—Ti bonds of $TiO_2$ in high concentration of NaOH solution are broken to form a six-coordinated monomer, $[Ti(OH)_6]^{2-}$. This monomer is highly unstable and thus prone to forming original nuclei. $Na_2Ti_nO_{2n+1}$ is subsequently grown around the formed nuclei. The difference in morphological rates of each crystallographic direction, leads to the formation of 1D $Na_2Ti_nO_{2n+1}$ nanowires [29]. The $Na_2Ti_nO_{2n+1}$ is then converted into $H_2Ti_nO_{2n+1}$ via acid washing and subsequently decomposed

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