



# Self-cleaning anti-fouling hybrid ultrafiltration membranes via side chain grafting of poly(aryl ether sulfone) and titanium dioxide



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## ABSTRACT

We report the fabrication and characterization of a novel organic/inorganic hybrid ultrafiltration membrane with anti-fouling and self-cleaning properties. Nanoscale TiO<sub>2</sub> clusters were grafted on the side chains of a poly(aryl ether sulfone) matrix containing trifluoromethyl and carboxyl groups (PES-F-COOH) using a silane coupling agent. Separation efficiency, fouling behavior, and self-cleaning property of the TiO<sub>2</sub>/PES-F-COOH hybrid ultrafiltration membrane were investigated by dead-end filtration experiments using a polyacrylamide foulant solution. Analysis of the membrane chemistry showed that grafting TiO<sub>2</sub> on the side chain of the PES-F-COOH resulted in homogeneous dispersion of TiO<sub>2</sub> clusters in the polymer matrix. The hybrid UF membrane exhibited significant self-cleaning efficiency. Specifically, water flux following polyacrylamide fouling was 53% recovered after membrane exposure to UV irradiation, which is attributable to photocatalytic degradation of the organic foulants by TiO<sub>2</sub>. We further demonstrated the anti-photocatalytic ageing property of the hybrid UF membrane, indicating resistance to decomposition of the membrane polymer matrix by photocatalytic oxidation. Our developed method can serve as a versatile platform for the development of anti-fouling and self-cleaning hybrid membranes or functional materials for a wide range of applications.

## 1. Introduction

Polyacrylamide (PAM), a linear water-soluble polymer, is widely used as a commercial flocculant for treatment of drinking water and municipal wastewater [1]. However, in recent years, concern has grown about the toxicity of PAM and its residual acrylamide (AM) monomers as well as their accumulation, migration, and transformation in the environment [2]. Accordingly, various separation methods to remove PAM from water have been widely studied [3].

Traditional separation methods for high-molecular-weight organic pollutants, such as chemical oxidation, often suffer from serious drawbacks, including high operating costs and formation of hazardous byproducts. Similarly, activated carbon adsorption faces challenges in separation and recovery of the adsorbents [4]. Biological treatment can also be used, but the process is limited by a slow degradation rate and low separation efficiency [5]. In contrast, membrane separation

provides an efficient solution to organic pollutant separation with unique characteristics, such as separation without phase change, competitive operating cost, relatively low energy consumption, and ease of operation and scale-up [6–9]. In particular, ultrafiltration has been demonstrated to be effective in retaining large organic macromolecules, such as PAM, from water [10,11].

However, membrane fouling is a major obstacle for widespread application of ultrafiltration [12]. Membrane fouling results in reduction of water flux and separation efficiency, which in turn reduces membrane lifetime and increases operating costs [6,13,14]. Various approaches have been attempted to reduce membrane fouling, including surface modification to impart membrane fouling resistance and optimization of hydrodynamic conditions [15]. Surface modification to increase membrane hydrophilicity appears to be effective at reducing organic foulant adsorption on the membrane surface [16–18]. A number of techniques have been explored for the preparation of highly

*Abbreviations:* AM, acrylamide; PAM, polyacrylamide; DFPS, 4,4'-difluorophenyl sulfone; HFID, 4,4'-(hexafluoroisopropylidene) diphenol; APTES,  $\gamma$ -aminopropyltriethoxysilane; PES, polyethersulfone; PPL, phenolphthalein; PVDF, polyvinylidene difluoride; F<sub>RR</sub>, flux recovery ratio; R, retention rate; R<sub>ir</sub>, irreversible fouling ratio; R<sub>r</sub>, reversible fouling ratio; R<sub>t</sub>, total fouling ratio; CA, contact angle; SEM, scanning electron microscopy; EDS, energy dispersive X-ray spectrometry; THF, tetrahydrofuran; UF, Ultrafiltration

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hydrophilic, fouling-resistant ultrafiltration membranes, including (i) surface grafting with anti-fouling polymers or nanomaterials [15,19–23], (ii) incorporation of hydrophilic organic substituents into the base polymer during membrane fabrication [24], and (iii) embedding hydrophilic inorganic nanoparticles into polymer matrices [15,25]. Among these methods, embedding inorganic nanoparticles into polymer matrices to fabricate hydrophilic composite ultrafiltration membranes could combine the advantages of inorganic and organic materials for enhanced anti-fouling property.

Titanium dioxide ( $\text{TiO}_2$ ) has long been recognized as an effective photocatalytic nanomaterial for degradation of organic contaminants in water treatment processes [26–28]. Several studies have demonstrated that membranes with  $\text{TiO}_2$  effectively immobilized degraded organic foulants, thus enhancing membrane separation performance. Incorporation of hydrophilic  $\text{TiO}_2$  nanoparticles in ultrafiltration membranes could therefore utilize the photocatalytic degradation ability of  $\text{TiO}_2$  to reduce membrane fouling [29–31], while overcoming the difficulty of recovering the  $\text{TiO}_2$  nanoparticles. Anderson et al. initially investigated the possibility of coupling photocatalytic  $\text{TiO}_2$  functionalization with membrane separation [32], which triggered a number of following studies that investigated the preparation of  $\text{TiO}_2$ -embedded membranes [33–35]. For example, Damodar et al. prepared modified polyvinylidene difluoride (PVDF) membranes by blending different amounts of  $\text{TiO}_2$  particles into the casting solution, and investigated their anti-bacterial, photocatalytic, and anti-fouling properties. They showed that  $\text{TiO}_2$  addition significantly affected pore size and hydrophilicity of the membrane, and consequently improved water permeability of the modified PVDF/ $\text{TiO}_2$  membrane.  $\text{TiO}_2$ -embedded PVDF membranes also exhibited anti-bio and -organic fouling abilities under UV light exposure [36].

Polyethersulfone (PES) is widely used in the preparation of commercial ultrafiltration membranes due to its excellent mechanical properties and thermal and chemical stability [37]. However, commercial PES ultrafiltration membranes are prone to fouling because of their hydrophobic nature. To overcome this limitation, Rahimpour et al. incorporated  $\text{TiO}_2$  particles into a PES ultrafiltration membrane via a solution blending method. They reported higher water fluxes for the  $\text{TiO}_2$ -embedded PES membrane under UV irradiation compared to the pristine PES membrane. In addition, the  $\text{TiO}_2$ /PES ultrafiltration membranes displayed self-cleaning property under UV irradiation attributed to the photocatalytic degradation of organic foulant by  $\text{TiO}_2$  [38].

However, direct introduction of inorganic  $\text{TiO}_2$  nanoparticles into polymer matrices by simple blending gives rise to a number of deleterious effects. For example, aggregation of inorganic  $\text{TiO}_2$  nanoparticles into large clusters in polymer matrices leads to dramatic reduction in photocatalytic activity of  $\text{TiO}_2$ . Moreover, due to the weak interactions between the base polymer and the  $\text{TiO}_2$  particles, the particles could be easily detached from the membrane during operation [39]. A strong chemical bonding between the inorganic  $\text{TiO}_2$  nanoparticles and polymer matrices could prevent such problems, allowing the preparation of hybrid ultrafiltration membranes functionalized with

homogeneously dispersed nanoscale  $\text{TiO}_2$  clusters.

In the present study, an anti-photocatalytic ageing poly(aryl ether sulfone) polymer matrix containing trifluoromethyl groups and carboxyl groups (PES-F-COOH) was synthesized through the copolymerization of phenolphthalein (PPL), 4,4'-(hexafluoroisopropylidene) diphenol (HFID), and 4,4'-difluorophenyl sulfone (DFPS).  $\text{TiO}_2$  clusters were then covalently linked to the side chains of the PES-F-COOH matrix using a silane coupling agent to produce a hybrid  $\text{TiO}_2$ /PES-F-COOH ultrafiltration membrane through phase separation technique. The separation, anti-fouling, and self-cleaning properties of the prepared  $\text{TiO}_2$ /PES-F-COOH hybrid ultrafiltration membranes were investigated using a polyacrylamide (PAM) foulant solution. Additionally, the anti-photocatalytic ageing properties of the hybrid ultrafiltration membranes were also evaluated.

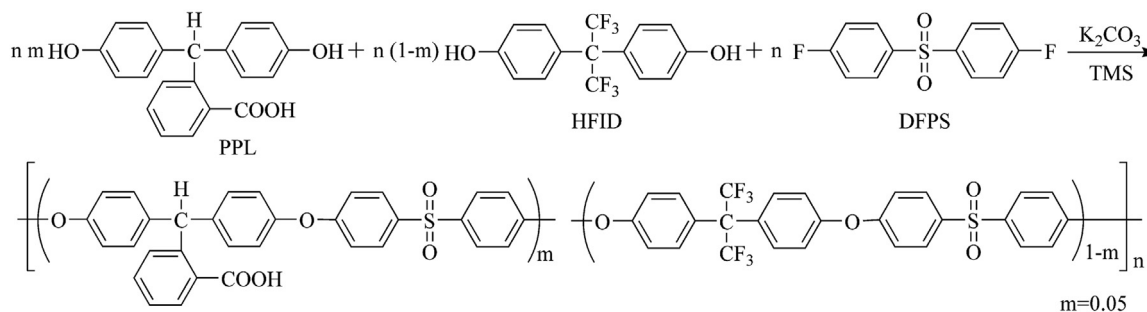
## 2. Materials and methods

### 2.1. Chemicals

Phenolphthalein (PPL) was purchased from TCI Shanghai Development Co. Ltd, China. 4,4'-(hexafluoroisopropylidene) diphenol (HFID) and 4,4'-difluorophenyl sulfone (DFPS) were obtained from Sigma-Aldrich (Shanghai Trading Co. Ltd., China). Polyvinylpyrrolidone (PVP), polyacrylamide (PAM,  $M_w$ :  $2.0 \times 10^6 - 1.4 \times 10^7$ ), and P25  $\text{TiO}_2$  were purchased from Aladdin Reagent (Shanghai Co. Ltd., China). Tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) were also acquired from Aladdin Reagent (Shanghai Co. Ltd., China) and further purified according to the standard procedures. Anhydrous potassium carbonate, toluene, and oxalyl chloride were provided by Sinopharm Chemical Reagent.  $\gamma$ -Aminopropyltriethoxysilane (APTES, KH-550) was supplied by Nanjing Fine Chemical Co. Ltd, China. Tetramethylene sulfone (TMS) was obtained from Jinzhou Oil Refinery and purified by distillation under reduced pressure. All other chemicals were reagent grade and used as received. Deionized (DI) water was used throughout the experiments.

### 2.2. Synthesis of PES-F-COOH polymer matrix

A fluorine-containing, anti-photocatalytic ageing PES-F-COOH polymer matrix was synthesized via aromatic nucleophilic substitution, as depicted in Scheme 1. PPL (0.32 g, 0.001 mol), HFID (6.39 g, 0.019 mol), DFPS (5.08 g, 0.020 mol), anhydrous  $\text{K}_2\text{CO}_3$  (2.90 g, 0.021 mol), TMS (36 mL), and toluene (20 mL) were added to a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet with thermometer, and a Dean-Stark trap with condenser. The mixture was heated to 120 °C under stirring. After two hours reaction under reflux, residual water and excess toluene were removed. The reaction temperature was then increased to 160–170 °C and maintained for six hours copolymerization. After cooling to room temperature, a viscous copolymer solution was poured into DI water to yield a flexible, threadlike polymer. This polymer was then pulverized



Scheme 1. Synthesis of the PES-F-COOH polymer matrix.

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