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## Hydrophilic photocatalytic membrane via grafting conjugated polyelectrolyte for visible-light-driven biofouling control

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## ABSTRACT

The photocatalytic membrane (PM) is a promising platform to impart membranes with an anti-biofouling property. However, the fabrication of effective PMs remains challenging because the physical loading of photoactive materials on the membrane can cause pore blocking and layer delamination due to repetitive operations. In this study, we demonstrate a chemical grafting of conjugated polyelectrolytes (CPEs) on a PVDF membrane surface to generate visible-light-active PMs with high stability. Using chemical tethering of CPE on the membrane followed by anion exchange, the surficial hydrophilicity of PM is improved significantly without compromising its porosity and water permeability. The hydrophilic PM exhibits excellent performance for photo-degradation of organic dyes, photo-reduction of Cr(VI), and photocatalytic inactivation of mixed-culture biofilm under visible light irradiation. The anti-biofouling property enables > 97 % flux recovery in repeated filtration cycles through the visible light treatment, even after it is fouled with a super-saturated bacterial feed solution (10<sup>9</sup> CFU/mL).

## 1. Introduction

Biofouling is a critical obstacle in membrane-based water treatment processes because it leads to a significant decrease in water flux and thereby causes increased energy consumption [1]. The accumulative bacterial adhesion on the membrane surface results in the growth of microbial cells, forming a biofilm as the major cause of membrane biofouling [2]. Conventionally, the fouled membranes are cleaned at regular intervals by chemical treatment [3] or backflushing [4]. However, such cleaning processes can damage the membrane surface due to harsh chemicals, leading to the reduction in membrane lifecycle. Many efforts have been made to mitigate biofouling by the surface modification of membranes [5], to name a few, control of hydrophilicity [6], roughness [7], and surface charge [8]. Among such strategies, surface coating of membranes with microbicidal materials is of interest to fabricate anti-biofouling membranes for sustainable water treatment [9]. In particular, the introduction of photocatalytic materials on the membrane surface is a promising approach to enable biofouling resistance as well as photo-degradation of organic contaminants in feed solutions [10].

In this regard, photocatalytic membranes (PMs) have been exploited by integrating commercial water purification membranes with various

photocatalysts [11]. Early examples focused on the fabrication of PMs with UV-responsive semiconductors, such as TiO<sub>2</sub> [12] and ZnO [13], and recently, visible-light responsive PMs were developed by using modified TiO<sub>2</sub> [14] and ZnO [15], β-FeOOH [16], and graphitic carbon nitride [17]. The photocatalyst dispersions were typically loaded on the membrane by vacuum filtration, providing the self-cleaning ability under light illumination. The physical loading of photoactive materials on the membrane, albeit easy to make, has drawbacks of pore plugging and layer delamination due to repetitive operations. Previously, such problems were tackled by blending photocatalysts within the membrane [18] or by producing free-standing PMs without membrane supports [19]. Nevertheless, issues of sophisticated preparation processes, production costs, and low mechanical strength remain unresolved [11]. The fabrication of visible-light-responsive PMs with high stability and performance is indeed challenging.

Conjugated polymers have emerged as a new class of visible-light-active heterogeneous photocatalyst [20]. By virtue of structural designability as organic polymers, the molecular composition of conjugated polymers determines their photophysical properties [21]. The side chain engineering of conjugated polymers allows for the fine-tuning of additional properties such as hydrophilicity/hydrophobicity [22], processability [23], and latent reactivity [24]. Conjugated polyelectrolyte

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