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# Star polymer-mediated in-situ synthesis of silver-incorporated reverse osmosis membranes with excellent and durable biofouling resistance

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## ABSTRACT

Biofouling mitigation for water purification membranes is critically important for the efficient separation process. Most anti-biofouling thin-film nanocomposite (TFN) membranes have been incorporated with biocidal nanomaterials via ex-situ hybridization, often leading to performance deterioration and ineffective nanomaterial incorporation. Here, we present a new in-situ hybridization strategy for the fabrication of silver-incorporated TFN (CD-Ag-TFN) reverse osmosis (RO) membranes exhibiting excellent anti-biofouling and separation performance by utilizing an amine-functionalized star polymer. CD-Ag-TFN membranes were formed by adding a Ag precursor ( $\text{AgNO}_3$ ) to an aqueous solution containing poly(acryloyl hydrazide)-branched star polymers (CD-PAHs) prior to interfacial polymerization with trimesoyl chloride (TMC). Numerous amine groups in CD-PAH strongly adsorbed  $\text{Ag}^+$  ions via complexation, which were subsequently converted to Ag or AgCl nanoparticles, while simultaneously forming a polyamide (PA) selective layer via the reaction with TMC, consequently creating a uniform PA-Ag hybrid network. Due to its greater hydrophilicity and high crosslinking density, the optimized CD-Ag-TFN membrane exhibited RO performance, which is better than that of the CD-PAH-assembled control (CD-TFC) and comparable to that of recently reported other lab-made RO membranes. Importantly, the robust and effective incorporation of Ag endowed the CD-Ag-TFN membrane with remarkably long-lasting anti-bacterial activity and greater anti-biofouling performance than control CD-TFC.

## 1. Introduction

Polyamide thin-film composite (PA TFC) membranes have been extensively explored as standard membranes for desalination and water treatment [1,2]. PA TFC membranes are synthesized by interfacial polymerization (IP) of diamine and acyl chloride (i.e., trimesoyl chloride, TMC) monomers dissolved in two immiscible solvents, which creates a nanoscale-thin polyamide (PA) permselective layer on a porous support [3]. Despite their high separation ability, PA TFC membranes suffer from biofouling by microorganisms due to their intrinsic surface structure and physicochemical properties [4].

Many efforts to endow membranes with biofouling resistance have been reported, including the incorporation of anti-fouling nanomaterials into and/or onto the PA layer and the chemical or topological modification of the PA surface [5–8]. In particular, membranes containing nanomaterials, referred to as thin-film nanocomposites (TFNs), have attracted considerable attention as a promising approach to mitigate biofouling because their functions can be readily tailored depending on the characteristics of the incorporated nanomaterials [9]. Various

nanomaterials, including silver (Ag) [7], metal organic framework [10], titanium dioxide [11], carbon nanotube [12] and copper [13], have been explored as functional fillers because of their strong biocidal effects.

Most TFN membranes have been fabricated through ex-situ hybridization, in which premade nanomaterials are added during the formation of the PA layer [14]. Although fabricated TFN membranes enhance biofouling resistance, inevitable nanomaterial aggregation and low PA–nanomaterial compatibility often weaken membrane performance and reduce the stability of nanomaterials [15,16]. To overcome these limitations, a very few in-situ hybridization methods, which simultaneously create the PA matrix and nanomaterials, have been proposed [4, 17]. Although the previously proposed in-situ hybridization methods effectively reduce nanomaterial aggregation, the lack of compatibility between the PA matrix and nanomaterials can impair the long-term stability of nanomaterials. Furthermore, the use of additives (i.e., reducing agents and stabilizers) is required to produce the nanomaterials, which may also adversely affect membrane performance [4]. Thus, a more effective and facile in-situ hybridization strategy needs to

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