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# Rationally designed in-situ fabrication of thin film nanocomposite membranes with enhanced desalination and anti-biofouling performance

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## ABSTRACT

Silver nanoparticle (AgNP)-incorporated thin film nanocomposite (Ag-TFN) membranes with enhanced reverse osmosis (RO) separation and anti-biofouling performance were fabricated via a rationally designed in-situ hybridization technique based on the dual action of reactant materials: (1) *m*-phenylenediamine (MPD) monomer, conventionally employed to form a polyamide (PA) selective layer, can also reduce Ag precursors ( $\text{AgNO}_3$ ) to form AgNPs; (2) sodium dodecyl sulfate (SDS) surfactant, widely used to facilitate PA formation, can also stabilize AgNPs and transfer them to the interface where the PA layer is formed. The simple addition of  $\text{AgNO}_3$  to an MPD solution containing SDS during interfacial polymerization enabled the simultaneous formation of the PA layer and AgNPs, which led to the uniform incorporation of AgNPs into the PA matrix, creating the PA-AgNP interfacial free volume (nanovoids) without impairing PA crosslinking. Hence, the Ag-TFN membrane exhibited remarkably higher water permeance with similar NaCl rejection in comparison with the pristine thin film composite (TFC) and commercial membranes, mainly owing to its enhanced interfacial free volume and increased hydrophilicity. The Ag-TFN membrane also exhibited better anti-biofouling performance than control TFC owing to the antibacterial ability of AgNPs and reinforced anti-adhesion enabled by its reduced surface roughness and enhanced surface hydrophilicity.

## 1. Introduction

Polyamide (PA) thin-film composite (TFC) membranes have been extensively employed in reverse osmosis (RO) processes to produce clean water [1–3]. PA TFC RO membranes are fabricated via interfacial polymerization (IP) between *m*-phenylenediamine (MPD, dissolved in an aqueous phase) and trimesoyl chloride (TMC, dissolved in an organic phase), yielding an ultrathin PA selective layer on a support [4]. Despite the excellent permselectivity of PA TFC membranes, there is still a strong need for mitigating membrane fouling (particularly biofouling) to enhance the process efficiency [5].

Numerous strategies to enhance the biofouling resistance of PA TFC membranes have been proposed, including chemical or topological surface modification and the incorporation of hydrophilic or antibacterial nanomaterials into or onto the PA selective layer [5–8]. Of these approaches, the nanomaterial-incorporated TFC membrane, referred to as thin film nanocomposite (TFN), has received significant interest because its separation performance and durability (fouling and oxidation resistance) can be effectively enhanced depending on the properties

of the incorporated nanomaterials [8–11]. A variety of nanomaterials, including silver (Ag) [7], zinc oxide [12], titanium dioxide [13], graphene oxide [8] and carbon nanotube [14], have been introduced into the PA layer to improve the biofouling resistance of the membrane.

Nanomaterials have typically been incorporated into the PA layer by adding premade nanomaterials to either the aqueous or organic phase before the IP process, which is referred to as ex-situ hybridization [15]. Although ex-situ hybridized TFN membranes exhibited enhanced anti-biofouling performance, the unavoidable formation of nanoparticle aggregates and/or the significant interference of the nanoparticles in the IP reaction created defects in the PA layer, reducing membrane separation performance [16–18]. The additional steps required for nanoparticle synthesis also complicated the fabrication process and rendered it less commercially viable [18]. Thus, it is necessary to develop a simple method for the fabrication of TFN membranes that offer excellent separation and anti-biofouling performance.

In-situ hybridization, in which the nanoparticles and polymer matrix are simultaneously formed to create a highly uniform hybrid network, has been extensively explored in many composite systems [15,19,20].

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