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## Thin film composite reverse osmosis membranes prepared via layered interfacial polymerization



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## ABSTRACT

Reverse osmosis (RO) process using a thin-film composite (TFC) membrane is a current leading technology for water desalination. The polyamide permselective layer of the TFC membrane enables salt retention and water permeation, with the ultimate goal of minimizing the permselective layer thickness for maximum energy efficiency. Yet this drive towards reducing the permselective layer thickness is greatly handicapped by the interfacial polymerization (IP) approach used to fabricate TFC membranes. We present layered interfacial polymerization (LIP) as a new paradigm for fabricating TFC membranes with unprecedented nanoscale control in the permselective layer thickness and smoothness, coupled with the advantage of industrial scale manufacturability. Membranes fabricated using LIP demonstrated high NaCl rejection necessary for water desalination, with water permeance  $\approx 86\%$  and permselectivity  $\approx 450\%$  greater than that of the membranes prepared using conventional IP and comparable water permeance and permselectivity  $\approx 17\%$  higher than that of commercial RO membranes. In addition, the unique smooth morphology of the LIP-assembled membrane surface enabled to mitigate the membrane fouling compared to the characteristic rough surface of the conventional IP-assembled membrane.

## 1. Introduction

Minimizing the energy footprint is one of the primary goals in water desalination. This motivation has led to the development of ultrathin permselective layers starting with cellulose acetate to the current aromatic polyamide (PA) thin film composite (TFC) membranes used in reverse osmosis (RO) membrane process today [1,2]. The permselective layer of the TFC membrane has been designed to selectively reject salts while permitting water, with the ultimate goal of minimizing the permselective layer thickness for achieving maximum energy efficiency [3]. Commercial PA TFC membranes are typically fabricated by interfacial polymerization (IP). This IP process begins with impregnating a porous polymeric support with an aqueous *m*-phenylenediamine (MPD) solution and subsequent exposure to an organic trimesoyl chloride (TMC) solution. The polymerization is diffusion-limited due to the high reactivity of the monomers leading to the rapid formation of a

dense PA layer, thus preventing further diffusion of MPD monomer to the TMC phase [4–7]. Although IP is a simple and scalable process capable of producing thin ( $\approx 100$  nm) PA layers, it is an empirical approach that limits our ability to control both the structure and chemistry of the PA layer [8]. Consequently, it is difficult to anticipate further reduction in energy consumption for water desalination using TFC membranes fabricated by IP due to its inability in separately optimizing the extrinsic (thickness and surface roughness) and intrinsic (chemistry and/or molecular structure) properties of the PA layer [9,10]. These limitations not only constrain the performance of current TFC membranes, but they also hamper our fundamental understanding of water desalination membrane structure-performance relationships [7,11].

In an effort to address the inherent limitation of IP, molecular layer-by-layer (mLbL) [12] was recently devised as an alternative approach for fabricating ultrathin TFC membranes with independent

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