



## Incorporating organic nanospheres into the polyamide layer to prepare thin film composite membrane with enhanced biocidal activity and chlorine resistance

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### ABSTRACT

To enhance the antibacterial property and chlorine resistance, organic nanospheres, polypyrrole (PPy), were innovatively incorporated into the polyamide (PA) layer for fabricating thin film nanocomposite (TFN) membranes. Owing to the improved hydrophilicity and compatibility between the PPy nanospheres and the PA layer, the obtained TFN membranes exhibited significant water flux enhancement without sacrificing salt rejection. Under the optimal PPy dosage (0.006 wt%), TFN membranes showed a high water flux of 42.19 L/(m<sup>2</sup> h), which was 118.0% higher than that of the pristine membrane. Remarkably, the chlorine resistance of TFN membranes was strengthened after the incorporation of PPy nanospheres, as evidenced by the less decreased salt rejection, as compared with the TFC and commercial RO membrane. In addition, the positively charged PPy nanospheres immobilized in the PA layer endow the TFN membranes with improved biocidal activity, which was much higher than that of the pristine membrane. This study shows that incorporating organic nanospheres into the PA layer is an effective strategy to develop new TFN membranes with enhanced performance for advanced water purification.

### 1. Introduction

Due to the severe industrial contamination and rapid population growth, global water scarcity and security have become critical problems [1,2]. Such concerns have made desalination, the process of removing salts and suspended solids from brackish water or seawater, a fast-growing technology for alleviating water scarcity. Reverse osmosis (RO), nanofiltration (NF) and forward osmosis (FO), based on thin film composite (TFC) polyamide membranes, play significant roles in desalination and wastewater treatment, owing to their outstanding performance (better selectivity and higher flux compared with asymmetric membranes) [3,4]. For example, RO is the most cost-effective and popular desalination technology [5] for producing potable water due to the recent advances in TFC membranes. Moreover, RO is easy to scale-up and could substantially slash the cost of desalination plants [6]. Presently, RO produces daily 86.5 Mm<sup>3</sup> potable water, which accounts for more than 50% of world desalination capacity [7].

However, TFC membranes still have some drawbacks, such as high biofouling propensity [8], low chlorine resistance [9] and the trade-off

between permeability and selectivity [10]. Particularly, the poor antibacterial property and low chlorine resistance cause frequent cleaning, reduced permeate quality and short membrane lifespan, which ultimately increases the operating costs [11]. To surmount these constraints, coating or grafting new ingredients with specific properties [12–14], introducing new aqueous or organic monomers [15–17] and using functionalized additives [18–20] were employed to develop new TFC membranes. Enlighten with the nanoscale design concept, integration of inorganic nanoparticles into the PA layer to fabricate thin film nanocomposite (TFN) membranes is a breakthrough in this field [21]. The advent of these intriguing TFN membranes could upgrade the antibacterial property and chlorine resistance compared with the conventional TFC membranes. Meanwhile, the incorporated nanoparticles can enhance the hydrophilicity of the membranes and affect the interfacial polymerization process, thereby improve the permeability and selectivity. Since the pioneering research by Jeong et al. who fabricated zeolite A based TFN membranes [21], a variety of inorganic particles, such as Ag [22], clay nanosheets [23], graphene oxide [24], carbon nanotube [25], metallic oxide [26] and composite metallic oxide [27]

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nanoparticles, were successfully embedded into the PA layer to design TFN membranes. These incorporated inorganic nanoparticles render TFN membranes with plural glamorous properties. For instance, Dong et al. [23] developed a TFN membrane with enhanced antifouling performance and permeability by adding montmorillonite and layered double hydroxide into the organic phase. Song et al. [6] fabricated a new graphene oxide quantum dot modified TFN membrane with antifouling property and chlorine resistance.

Although excellent properties have been obtained with the incorporation of inorganic nanoparticles, the poor affinity between polymers and inorganic nanoparticles tends to form non-selective voids, which deteriorates the selectivity [28,29]. Chemical modification of inorganic nanoparticles has witnessed its success in improving their compatibility with the polymers in PA layer [30,31]. However, chemical modification processes are tedious and complicated, and thus impede their popularity. Metal organic frameworks (MOFs), act as a type of multifunctional organic-inorganic composites, possess better miscibility with polymer matrix and have been utilized as fillers to design new TFN membranes [29]. Nevertheless, many MOFs are unstable in water or hydrophobic [32]. Organic materials are known to have better compatibility with polymers compared with inorganic or organic-inorganic hybrid materials. Covalent organic frameworks (COFs) are a burgeoning series of organic composites assembled via covalent bonds, have shown their compatibility in TFN membranes [33]. However, their tedious and harsh synthesis conditions and high costs impair the applications. Therefore, it is imperative to seek cost-effective and multifunctionalized nanomaterials with good compatibility to design next-generation TFN membranes for advanced water purification.

Polypyrrole (PPy), as a distinct polymeric material, has prevailed in commercial applications due to its well conductivity and excellent biocompatibility [34]. The organic nature of PPy promotes its miscibility with polymeric matrix. Additionally, PPy has the low cost, outstanding processability and water stability, making it superior to many inorganic nanofillers. Based on these properties, PPy nanospheres have been incorporated into PSf membranes for ultrafiltration [35]. Appealing results, such as extraordinary water flux and charged surface were achieved. The good miscibility of PPy nanospheres led to the improved porosity and interconnected structures of ultrafiltration membranes. When PPy nanospheres are introduced to TFN membranes during interfacial polymerization, strong bonds (e.g. hydrogen bond and amino bond) exist between the PA substrate and PPy nanospheres with abundant chemical groups (amine groups), which may result in stable structures and excellent membrane performance. More interestingly, PPy is an excellent biocidal polymer [36,37], which could contribute to the antibiofouling property of the membrane. The antioxidant activity of PPy may also enhance the chlorine resistance of the membrane [38]. However, PPy nanospheres have not been used to fabricate new TFN membranes so far.

Herein, for the first time, we innovatively incorporated facile-synthesized organic nanospheres (PPy) into the PA layer to fabricate well-compatible TFN membranes with excellent antibacterial property, chlorine resistance and permeability. The separation performance of the membranes was investigated by water flux and salt rejection. The antibacterial property was investigated by measuring the growth status of bacteria on the membranes, and the chlorine resistance was evaluated by comparing the separation performance of membranes before and after soaked in sodium hypochlorite solutions. Thanks to the totally

organic attribute and intrinsic rich amino group of PPy, the obtained composite membrane indicates improved water flux, elevated salt rejection, increased antimicrobial property and chlorine resistance. This study provides a new strategy for developing TFN membranes with enhanced performance.

## 2. Experimental

### 2.1. Materials

Commercial polysulfone (PSf) support membrane (MWCO: 20 kDa) was purchased from RisingSun Membrane Technology Co., Ltd. (China). Commercial RO membrane was obtained from Koch membrane systems (America). Pyrrole and trimesoyl chloride (TMC) were provided by Aladdin Co., Ltd (China). 2,4-diaminodiphenylamine was supplied by Shanghai Titan Scientific Co., Ltd (China). Ferric chloride ( $\text{FeCl}_3$ ), methanol and triethylamine (TEA) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). *m*-Phenylenediamine (MPD), (+)-10-camphorsulfonic acid (CSA) and sodium hypochlorite ( $\text{NaClO}$ , 6%-10% free chlorine) were received from J & K Chemical Reagent Co., Ltd. (China). Sodium chloride ( $\text{NaCl}$ ) was purchased from Nanjing Chemical Reagent Co., Ltd. (China). *n*-Hexane was obtained from Merck Chemical Reagent Co., Ltd. (Germany). The purities of all chemicals are above analytical grade, and used without further purification. In all experiments, deionized (DI) water was supplied by a Millipore water purification system.

### 2.2. Preparation of PPy nanospheres

The preparation of PPy nanospheres was conducted based on the reported procedure (Fig. 1) [34]: 50 mg pyrrole and 15 mg 2,4-diaminodiphenylamine (initiator) were dissolved in 30 mL methanol under vigorous stirring, 120 mg  $\text{FeCl}_3$  was dissolved in 1 M hydrochloric acid with equivalent volume of methanol, and the suspensions were detached by suction filtration. Then the two solutions were refrigerated to 0 °C and promptly mixed. The reaction happened with handshaking for about 10 s and the mixture was kept overnight with no disturbance. The synthesized PPy nanospheres were centrifuged and purified at 4500 rpm/min with a mixture of DI water and methanol (9:1 in volume ratio). After that, a black powder was acquired and dried at 50 °C for three days before use.

### 2.3. Preparation of TFC and TFN membranes

TFC membranes were prepared on PSf ultrafiltration membranes support via interfacial polymerization [27]. The PSf membranes were washed and immersed in DI water for 24 h before use. The top surface of the membrane was rolled with a rubber roller and air dried at ambient temperature for 5 min, then the dried membrane was immobilized into a rubber frame. A certain amount of aqueous solution containing 2 wt% MPD, 2 wt% CSA and 2 wt% TEA was poured onto the surface of membrane and saturated for 2 min. The redundant aqueous solution was drained off and rolled back. After that, the membrane was air dried for another 5 min. An organic solution containing 0.1 wt% TMC in *n*-Hexane was gently spread on the membrane to react for 1 min. The excess organic solution was poured out and the membrane was air dried for 30 s. The prepared TFC membrane was cured at 60 °C for 10 min for further crosslinking. Finally, the membrane was stored in DI water for

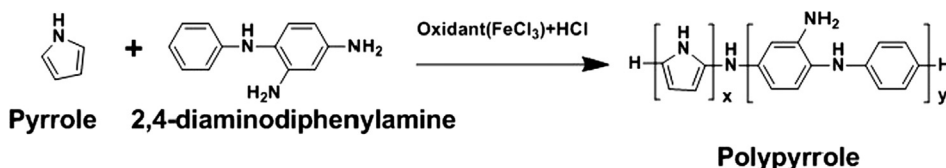


Fig. 1. Preparation of PPy nanospheres.

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