



# Fabrication of antifouling reverse osmosis membranes by incorporating zwitterionic colloids nanoparticles for brackish water desalination



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## ABSTRACT

Antifouling is important for RO membranes. Taking advantage of the reaction between hydroxyl groups on zwitterionic colloid nanoparticles (ZCPs) and acyl chloride group, ZCPs with tuned chemical structures were added into *m*-phenylenediamine aqueous solution to prepare thin-film nanocomposite membranes (ZPMs) via interfacial polymerization in this study. The incorporation of ZCPs tailored the membrane surface morphology and chemical properties, which were characterized by SEM, AFM, WCA, FTIR and XPS. Meanwhile, the effect on RO membranes separation and antifouling performances were systematically evaluated. In comparison with pristine membranes, the values of WCA decreased which means the hydrophilicity of membranes surface enhanced due to the existence of ZCPs, endowing the membrane with advanced water flux ( $37.3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ) when operate with 2000 ppm NaCl aqueous solution at 25 °C under 1.5 MPa. In order to evaluate the antifouling properties, the filtration with different types of model foulants were operated. When feed solution containing tannic acid, sodium alginate or sodium dodecyl sulfonate respectively as model foulants, ZPMs exhibited low water flux reduction and high water flux recovery after cleaning due to increased hydrophilicity and surface smoothness. Therefore, the ZPMs with improved separation and antifouling performances are promising candidates for practical application in brackish water desalination.

## 1. Introduction

The demand of fresh water is accelerated continuously over the past decades with the population overgrowth and water pollution [1,2]. Hence, the sustainable supply for fresh water plays a critical role in the current global development and membrane-based desalination technologies, such as nanofiltration (NF), reverse osmosis (RO), forward osmosis, etc., have been considered as promising solutions [3]. RO is the state-of-the-art technique for producing high quality fresh water from brackish water and seawater with eco-friendliness and effectiveness, which expected to reach 38 billion m<sup>3</sup> per year by 2016 [4]. Currently, the predominant thin-film composite (TFC) RO membranes used aromatic polyamide as selective layer have excellent separation performances [5,6]. Nevertheless, given problems of the cost in the application, there are a lot of researches focused on RO membranes materials to achieve low surface fouling tendency.

In order to mitigate the membrane fouling, a plenty of strategies have been raised to modify RO membranes such as hydrophilicity improvement and smooth surface construction. Some researchers developed different new interfacial polymer monomers or additives to

make membrane surface more hydrophilic, such as 5-isocyanatoisophthaloyl chloride [7], *N*-aminoethyl piperazine propane sulfonate [8], *o*-amino-benzoic acid-triethylamine [9]. In particularly, zwitterionic materials with the possession of both negative and positive charged units, present strong hydrophilicity which lead to the formation of strong and stable hydration layer [10,11]. For example, Shafi et al. [12] deposited copolymer films with zwitterionic structures on RO membrane surface, resulting in membranes exhibited almost 98% reduction in bacterial adhesion. Therefore, zwitterion-based materials are effective to achieve antifouling properties when applied into desalination membranes. Moreover, nanostructure materials including zeolite [13], silver particles [14,15], carbon nanotubes [4,16], graphene oxide [17,18], and aquaporins proteins [19,20], may provide a new route to address fouling issues [21,22]. Fabrication of thin-film nanocomposite (TFN) membranes with nanostructure materials could tailor the membrane selective layer features to achieve improved performance. Zhao et al. [16] incorporated carboxy-functionalized multi-walled carbon nanotubes into polyamide to fabricate TFN RO membranes to make membrane surface higher hydrophilicity and negative charge, which result in improved antifouling properties for

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inorganic and protein model foulant with nearly two times of initial water flux. Safapour et al. [17] prepared TFN membranes with embedding reduced graphene oxide/TiO<sub>2</sub> to improve RO membranes anti-biofouling properties for bovine serum albumin with increased separation performance. The better antifouling properties of the modified membranes result from their greater hydrophilicity, charge density and smoothness [23]. The aforementioned instances illustrated that the application of TFN RO membranes would expand in water desalination due to antifouling properties and greater permeability to promote economic effectiveness. Based on the previous researches, the nanoparticles associated with hydrophilic component introduced into RO membranes could confer improved antifouling and separation performance. However, these inorganic nanomaterials have inferior compatibility with polyamide matrix, which would lead to the destroyed stability of selective layer [4,23]. Recently, Ji et al. [24] exploited organic nanoparticles (zwitterionic polyelectrolyte complex nanoparticles, ZPNPs) which prepared through ionic cross-linking between poly (2-methacryloyloxy ethyltrimethylammonium chloride) and sodium carboxymethyl cellulose into polyamide selective layer to improve the water flux for NF. It manifested that the introduction of organic nanoparticles with zwitterionic groups could fabricate TFN NF membranes to achieve favorable performances. It is also shown that organic nanoparticles with flexible polymer backbone are beneficial to reduce the defects between particles and polyamide matrix.

Zwitterionic polymer would be assembled into colloid particles with zwitterionic chemical structures [25–27]. In our previous work, the zwitterionic colloid nanoparticles (ZCPs) synthesized by free radical polymerization have been used to prepare membranes by solution casting technique and followed by chemical cross-linking to achieve exceptional NF separation performance [27]. Nevertheless, the particle sizes of ZCPs exploited for these NF membranes are ~600 nm when present optimum performance [27]. These particles could not be applied into RO membranes which required denser polyamide layer than that for NF process. In this study, copolymerized ZCPs with tuned particle sizes by change reaction conditions were introduced into polyamide selective layer as organic nanoparticles via interfacial polymerization by the reaction between possessive hydroxyl groups and acyl chloride group to fabricate nanocomposite RO membranes (ZPMs), which would maintain stability of the selective layer [28]. This easy and effective method could introduce zwitterionic moiety and nanocomposite structure to selective layers. As a result, resulting membranes are able to achieve outstanding fouling-resistant and easy-cleaning properties. The hydrophilicity of zwitterionic group could promote the transport of water molecules and form hydration layer to prevent organic foulants from adhesion on membrane surface. And to our best knowledge, there are no RO membranes prepared by incorporating organic nanoparticles. The effects of ZCPs loading on the membrane surface physicochemical properties and perm-selectivity were systematically discussed. Moreover, antifouling performances of different foulant models were investigated to evaluate their potential practical application in brackish water desalination.

## 2. Experimental

### 2.1. Materials and reagents

1, 3-propanesultone (1, 3-PS) and *N*-aminoethyl piperazine (AEP, 99%) were received from TCI (Shanghai) Development Co., Ltd. 2-hydroxyethyl acrylate (HEA) was obtained from Shanghai Aladdin Reagent Company. 3-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate (DMAPS) using as the zwitterionic monomer for ZCPs preparation was synthesized based on our previous publication [29]. Potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and sodium bisulfite (NaHSO<sub>3</sub>) (ACS reagent) were received from Sigma-Aldrich Co., Ltd. 1,3-phenylenediamine (MPD, 99.5%) and trimeric acid trichloride (TMC, 99%) were obtained from Shanghai Aladdin Reagent Company. Triethylamine

(TEA, liquid, 99%) was obtained from Sigma-Aldrich Co., Ltd. Hexane and acetone used as organic solvent were analytical grade and obtained from Sinopharm Reagent Co., Ltd. Sodium chloride (NaCl, analytical reagent) was purchased from Sinopharm Reagent Co., Ltd. Foulant models used in fouling experiment that are tannic acid (TA, reagent grade), sodium alginate (NaAlg, bio reagent grade, Mn: 32,000–250,000) and sodium dodecyl sulfonate (SDS, reagent grade) were purchased from Sigma-Aldrich Co., Ltd. and Shanghai Aladdin Reagent Company respectively. All these reagents were used directly without any further purification. Deionized water (18 MΩ cm) was used in this study. Polysulfone ultrafiltration supporting membranes (PSf, molecular weight cut-off ~20 kDa) were supported by the Development Centre of Water Treatment Technology, Hangzhou, China.

### 2.2. Preparation of zwitterionic colloid nanoparticles

The ZCPs were prepared by HEA and DMAPS via free radical polymerization according to our previous publication [27]. The entire quantity of 2.5 g of monomers HEA and DMAPS with different mass ratio (DMAPS:HEA in ratio of 2:1, 3:1, 4:1, 5:1 and 6:1 respectively) were dissolved and stirred in 10 mL deionized water. And then the initiators, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2 mg) and NaHSO<sub>3</sub> (2 mg), were added into aqueous solution after purging with nitrogen (30 min, room temperature). The polymerization reacted at 40 °C for 1.5 h with stirring. Afterwards, the ZCPs were precipitated by acetone, and then freeze-drying to obtain products. The obtained ZCPs were named as ZCP1, ZCP2, ZCP3, ZCP4 and ZCP5 respectively according to the ratio of zwitterionic monomer DMAPS increased in total monomers.

### 2.3. Preparation of the membranes

The fabrication process of RO membranes are shown in Fig. 1, which were via interfacial polymerization. Firstly, pouring the MPD-water solution on the Psf surface and soaked for 2 min, and then removing the extra solution on supporting substrate surface. The MPD-water solution contained MPD:TEA in ratios of 2.0:1.0 wt% and certain amounts of ZCPs. Subsequently, the monomer saturated supporting substrate was soaked in a 0.10 wt% TMC-hexane solution for 1 min to induce forming a polyamide layer on the substrate surface. The prepared membranes were heat cured at 50 °C for 10 min, and then rinsed by deionized water. Finally, these membranes stored in opaque containers of deionized water until tests and characterizations.

### 2.4. Characterization of ZCPs

Fourier transform infrared spectroscopy (FTIR, Bruker Vector-22, Germany) and X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Scientific, USA) were used to performed the chemical structures and compositions of ZCPs. The morphologies of ZCPs were evaluated by field emission scanning electron microscopy (SEM, S4800, HITACHI, Japan). The ZCPs samples for SEM were prepared by deposition of 0.1 wt% dispersion solution on silicon wafers, and then frozen dry. The particle size and zeta potential of ZCPs were determined by dynamic light scattering (DLS, 90 Plus/BI-MAS, USA) using 0.1 wt% dispersion solution which were only pre-filtered by using a microfiltration membrane with pore size of 2 μm.

### 2.5. Membrane characterization and separation performance assessment

The membrane samples for all characterizations were washed by deionized water and drying at ambient atmosphere for 24 h before all characterizations. Chemical structures and compositions of membranes were characterized by FTIR and XPS. The membrane samples for FTIR analyzed were prepared without support layers. The morphology of RO membranes surface were evaluated by SEM directly. All SEM samples of membranes were sputter coated with gold. The membrane surface

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