



# Water/salt transport properties of organic/inorganic hybrid films based on cellulose triacetate



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## ABSTRACT

The synergized optimization of water flux and salt rejection by blending with inorganic fillers has been achieved for the polyamide (PA) thin film nanocomposite (TFN) membrane. However, it is difficult to characterize its mass transport properties due to the very thin and heterogeneous PA film. In this work, we select cellulose triacetate (CTA) as the base to prepare hybrid films and their transport properties were studied according to solution-diffusion theory. A series of inorganic fillers, such as reduced graphene oxide (RGO), zeolites, ZIF-8, SiO<sub>2</sub> and graphene oxide (GO) were incorporated. The SEM and EDX results indicate a less than 1 wt% filler content for a uniform dispersion. The blending of inorganic fillers leads to enhanced glass transition temperature ( $T_g$ ) and density, little effect on the water transport property but dramatically decreased salt permeability values, which are nearly ten-fold of that of the CTA film. The blending of GO can densify and hydrophilize CTA simultaneously, which is most promising for a desalination application. The increased water uptake should contribute to its increased water permeability, while the decreased free volume size and FFV value and various interactions between the ions (Na<sup>+</sup>, Cl<sup>-</sup>) and GO sheets account for salt permeability decrease.

## 1. Introduction

Great efforts have been made to enhance the desalination performance of the reverse osmosis (RO) membrane, which mostly refers to the permeability and selectivity of the desalting polymeric layer, for further decreasing the cost of the RO technology. Recently, it has been recognized that there is an empirical trade-off between the water permeability and water/salt selectivity of the polymeric membranes [1]. In fact, the trade-off relation widely occurs between the membrane permeability and the selectivity for both liquid and gas separation membranes. This relation defines the membrane performance and has attracted great attention from both the material and chemical engineering researchers [2]. In 1991, Robeson proposed that in the selectivity versus permeability plot for polymeric gas membranes, the data of a specific gas pair lie on or below the straight line, which was later on defined as the Robeson upper bound trade-off curve [3,4]. To overcome the upper bound trade-off limitation, a lot of attempts have been made on various novel membrane materials. As a result, significant progress has been made on the performance of the membrane materials, with organic/inorganic hybrid membrane as a milestone. The organic/inorganic hybrid membrane usually comprises of an organic polymer phase and an inorganic fillers phase. The hybrid membrane can

combine the cost effectiveness and easy process ability of the polymer enabling large-scale production, with inherent superior separation characteristics of the inorganic fillers [4,5]. The organic/inorganic hybrid membranes have been extensively visited for gas separation and pervaporation. Many of them show excellent separation properties, which are usually much superior than that of the corresponding pure polymer membrane [6]. With appropriate choice of polymer material and inorganic fillers, the organic/inorganic hybrid membranes frequently overcome the upper bound of pure polymeric material and become attractive for industrial production [7].

Encouraged by the work on organic/inorganic hybrid membranes for gas separation and pervaporation, Hoek and his coworkers reported a new concept of thin film composite (TFN) membrane by incorporating inorganic fillers into the polyamide (PA) layer to form nanocomposite thin films via the interfacial polymerization (IP) on a porous polysulfone (PSf) support. The zeolite nanoparticles were embedded into the PA layer prepared by the interfacial polymerization between *m*-phenyldiamine (MPD) and trimesoyl chloride (TMC). Compared to the pure PA TFC membrane, the resulted TFN membranes showed dramatically improved water flux without sacrifice of the salt rejection [7]. Since then, similar type of TFN RO membranes have been widely studied, and a variety of nanoparticles have been embedded into the PA

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layer. Among them are Ag nanoparticles, multi-walled carbon nanotubes (MWCNTs) and so on. Quite a few TFN membranes show high water flux, high salt rejection, as well as superior antibacterial or antifouling properties [8–10]. In fact, the TFN membrane not only attracts academic attention, but also leads to appealing commercial success. The water flux of the NanoH<sub>2</sub>O PA TFC RO membranes was twice as high as that of the conventional PA RO membranes and the NaCl rejection was maintained at 99.7% [11,12]. At present, the application of the TFN membrane is not just limited to aqueous membrane separation processes, such as nanofiltration (NF), reverse osmosis (RO) and forward osmosis (FO), but also extends to organic solvent filtration, gas separation and pervaporation processes. However, in spite of the superior desalination performance of the TFN membrane, the mechanism of improving the membrane desalting performance by adding inorganic fillers was not well understood, because the measurement of the fundamental water and salt permeability properties of the functional layer of TFN membranes is challenging due to the very low film thickness and the presence of gradient in composition and degrees of cross-linking in the PA layer [13–15].

Cellulose acetate was the earliest RO membrane developed by Loeb and Sourirajan in the 1970s [16]. In the last two decades, many technical constraints have been broken through. As a result, cellulose triacetate (CTA) hollow fiber membranes have dominated seawater desalination market in the Middle East. Compared with the mainstream polyamide TFC RO membranes, CTA membrane enjoys better oxidation resistance and better fouling resistance. More importantly, CTA can be fabricated into dense films enabling the collection of accountable water and salt transport data.

In this work, in view of the unclear mechanism of enhanced TFC membrane performance compared to pure TFC PA membrane and in order to have a better understanding of the effect of inorganic fillers on water and salt transport properties of polymeric membrane, CTA was selected as the continuous bulk phase to fabricate dense film for water and salt transport measurement. A series of hybrid films were casted by embedding different inorganic particulates, including reduced graphene oxide (RGO), ZSM-5 zeolite, MCM-41 zeolite, zeolite imidazole (ZIF-8), SiO<sub>2</sub> and graphene oxide (GO) etc. Their water and salt transport properties were investigated in details. The results are expected to shed light on the mechanism of the enhanced desalting performance of the TFN membrane. In addition, since the CTA membrane usually shows low salt rejection compared to the TFC spiral-wound membrane, the research on inorganic/organic hybrid membranes based on CTA may also provide opportunities for the development of high salt rejection CTA RO membrane.

## 2. Experimental

### 2.1. Materials and reagents

Cellulose triacetate (CTA,  $M_w = 350,000$ ) was purchased from Acros Organics. RGO, ZSM-5 zeolite (Si/Al: 350–400), MCM-41 zeolite (pure Si type) and SiO<sub>2</sub> were purchased from Nanjing XFNAO Materials Tech Co., Ltd, (Nanjing, China). GO was purchased from Suzhou Hengqiu Graphene Technology Co., Ltd. (Suzhou, China). Zeolite imidazole (ZIF-8) was prepared by a “direct mixing” synthesis strategy, i.e., directly mixing 2-methylimidazole (2-mIn) and Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution under vigorous stirring, according to the literature [17]. 1,4-dioxane and NaCl were supplied from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). De-ionized (DI) water was obtained from a Millipore MilliQ system (18.2 MΩ<sup>-1</sup> cm, 1.2 ppb TOC, pH = 6.9). Reduced graphene oxide (denoted as RGO) has the oxygen functional groups largely reduced, lamellar diameter of 30 nm and specific surface area (SSA) of 103 m<sup>2</sup>/g. Graphene oxide nanosheets are 3.4–7.0 nm thick (denoted as GO) and have 6–10 layer, a lamellar diameter of 10–50 μm, a SSA of 100–300 m<sup>2</sup>/g and a d-spacing of 7.89 Å (calculated by the Bragg picks of GO XRD patterns in Fig. S1). The basic properties

**Table 1**  
The basic properties of the inorganic fillers.

Type	The average particle size	Pore diameter	The specific surface area (SSA) <sup>a</sup>	The bulk density
ZSM-5	2.0 μm	0.53–0.58 nm	406 m <sup>2</sup> /g	0.30 g/mL
MCM-41	200 nm to 1 μm	5–6.0 nm	958 m <sup>2</sup> /g	0.15 g/mL
ZIF-8	300 nm	0.35 nm	1701 m <sup>2</sup> /g	0.34 g/mL
SiO <sub>2</sub>	20 nm	1.8 nm	141 m <sup>2</sup> /g	0.06 g/mL

<sup>a</sup> The SSA value was obtained by the BET analysis.

of other inorganic fillers were listed in Table 1. We note here that all the SSA values were obtained by the BET analysis on an Autosorb-iQ-c volumetric adsorption analyzer (Quantachrome Instruments, USA). The Nitrogen adsorption isotherms of the inorganic fillers and related discussions have been shown in Fig. S3 in the supplementary material.

### 2.2. The preparation of organic/inorganic hybrid films

The inorganic fillers were dispersed by mixing a certain weight of inorganic fillers (RGO, ZSM-5, MCM-41, ZIF-8, SiO<sub>2</sub> or GO) with 10 mL of 1,4-dioxane and sonicated for 1 h. A uniformly dispersed mixture was obtained. After that, CTA and a certain weight of 1,4-dioxane were added into the mixture to form an 8 wt% dispersion. After 12 h of vigorous mixing, the dope solution was thoroughly degassed overnight. The hybrid film was prepared by casting this solution with a doctor blade on a smooth glass substrate. The glass plate and the film were covered with a lid and kept at room temperature overnight to allow the solvent to evaporate. The film and the glass plate were then placed in a vacuum oven at 80 °C for 5 h to remove the residual solvent. After that, the film was peeled off from the glass plate. In this work, two types of freestanding dense film were prepared. The first type has a film thickness of about 100–200 μm, and was used for water and salt sorption (partition) coefficient testing; the second type (15–20 μm) was thinner and used for permeability testing. The preparation process of the organic/inorganic hybrid films is shown in Fig. 1.

### 2.3. The characterization of the organic/inorganic hybrid films

The surface morphology of the organic/inorganic hybrid films was investigated by the thermal field emission scanning electron microscopy (TESEM, ZEISS, Germany) and energy dispersive X-ray (EDX) analysis. Imaging was carried out at a voltage of 10 kV at a working distance (WD) of 8.0 mm. The magnification is 12–2,000,000 ×. The differential scanning calorimetry (DSC, DSC204F1, Netzsch, Germany) was used to determine the glass transition temperature ( $T_g$ ) of the hybrid films. Samples of 10 mg were sealed in an aluminum pan and were heated under N<sub>2</sub> atmosphere over a temperature range of 25 °C to 300 °C at the heating rate of 10 °C/min.

The free volume in the hybrid films was measured on a positron annihilation lifetime spectroscopy (PALS, EG&G ORTEC, USA) with a fast-fast coincidence system at the Institute of High Energy Physics of Chinese Academy of Sciences. The samples were equilibrated in DI water or 1 mol/L NaCl solution to their fully hydrated state before the measurement was conducted at ambient atmosphere. The position source (<sup>22</sup>Na, radioactivity 4.81 × 10<sup>5</sup> Bq) was sandwiched between two pieces of the hydrated films (1 × 1 cm<sup>2</sup>), which were stacked to a thickness of 1 mm. The time resolution was 196 ps and the probe material was BaF<sub>2</sub>. The spectrum was resolved with the LTv9.0 software with the fitting factors controlled between 0.9 and 1.1 [18]. According to the concept of the free volume, the free volume is the static space formed by the inefficient packing of polymer segments and the dynamic space occupied by the thermal motion of the segment [19]. Therefore, the free volume can be divided into the network cavity between molecular chains and the aggregation cavity between molecular associations including the interface between the fillers and the CTA polymer

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