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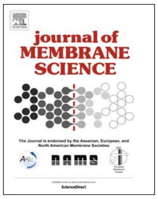

Influence of hydrophilic carbon dots on polyamide thin film nanocomposite reverse osmosis membranes

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ABSTRACT

There is critical to fabricate reverse osmosis (RO) membranes with high water-solute selectivity, thereby decreasing the energy input required in desalination processes. To achieve this, a super hydrophilic nano Carbon Dots (CDs) with quantum size of 6.8 nm was self-synthesized and successfully incorporated into the selective layer of polyamide (PA) thin-film nanocomposite (TFN) RO membrane. The novel CDs-TFN RO membrane was fabricated by dispersing the CDs nanoparticles at varying quantities into aqueous solution through interfacial polymerization (IP) of monomers of m-phenylenediamine (MPD) and trimesoyl chloride (TMC). Using Excitation and emission matrix (EEM) to explore the incorporation of CDs into the membrane skin layer, we observe that the fluorescence properties of CDs-TFN membrane decreased in order of increasing CDs concentration in relation to the unmodified TFC RO membrane which has the highest fluorescence count. The surface morphology of all TFN membranes transform from a leaf-like structure into ridge-and-valley structure with increased roughness, which has an important implication for flux enhancement. The TFN membrane with 0.02 wt% CDs incorporation exhibited promising desalination performance with water flux of 87.1 L/m^2/h and salt rejection of 98.8% than the control thin film composite (TFC) membrane (2000 ppm NaCl solution, 25 °C, 1.55 MPa). The improved performances of CDs-TFN membrane were attributed to the enhanced hydrophilicity, decreased thickness as well as the increased density of the selective layer due to the incorporation of small amounts of CDs nanoparticles. By extending the deposition time of CDs on the polysulfone substrate, the membrane performance was further improved with water flux of 88.7 L/m^2/h and salt rejection of 99.0%.

1. Introduction

Progressively increasing world's population and expanding development of agriculture and industry continues to pose enormous challenge on water resources which is crucial to the survival of human beings and the development of world economies [1]. Considering the high process-ability, low cost, as well as the flexibility of membrane systems, reverse osmosis (RO) is currently the most widespread desalination technology for producing high-quality water from sea water, brackish water and non-traditional water sources [2,3].

Thin-film-composite (TFC) polyamide (PA) membranes dominate the RO membrane market for water desalination, and are typically fabricated using monomers of m-phenylene-diamine (MPD) and monomers of trimesoyl chloride (TMC) through interfacial polymerization [3,4]. However, the highly cross-linked networks and hydrophobic aromatic materials inherently limit water flux efficiency [5]. Moreover, permeability-selectivity trade-off issues for nonporous polymeric membranes deters RO membrane separation performance [6]. This implies that a higher water permeation will often result in a lower salt rejection. Meanwhile, a highly selective membrane is of great significance in improving water quality and eliminating additional separation stages in water desalination, which if successful will represent an important advancement in next-generation RO membrane [7]. Therefore, there is a current pressing need for fabrication of membranes with high water- solute selectivity properties [8].

In 2007, Jeong et al. [9] were the first to report the concept of thin-film-nanocomposite (TFN) membrane by adding hydrophilic NaA zeolite nanoparticles into the matrix of PA films, which opens up a new research direction for the modification of membranes. The newly developed TFN membrane exhibited higher water flux and maintained a steady salt rejection. Recently Kah et al. [3] proposed the use of nanocomposite membranes, which offers the merits of increased flux and improved desalination. Moreover, considerable number of research have been dedicated to introducing functional nanoparticles into

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polymeric membranes, such as carbon nanotubes (CNTs) [10–12], graphene oxide [13,14], silica [15–17], TiO_2 [18], zeolite [9,19,20], alumina [21], metal-organic frameworks [22] and POSS [23,24]. The detailed nanofiller properties and relative desalination performances of the modified TFN membranes are summarized in Table S1.

Matrix-particle compatibility plays a key role in the incorporation of nanofillers into PA membrane to improve the membrane desalination performances [14]. In a more recent research, Duan et al. [22] incorporated hydrophobic metal-organic framework (MOF) ZIF-8 into PA layer of TFN membrane. Compared with classic hydrophilic zeolite, the ZIF-8 exhibited better compatibility due to the imidazolate linker addition, which increases compatibility between the inorganic ZIF-8 and organic PA matrix. The resultant membranes showed 162% increased water permeability than the pristine membrane but maintained NaCl rejection. Multi-walled carbon nanotubes (MWNTs) are intrinsically hydrophobic and have been employed in the fabrication of TFN RO membrane by acidifying the MWNTs, which showed a slightly improved dispersion in MPD solution [25]. The as-prepared membranes achieved increase in water flux with an accompanying decrease in salt rejection. Other works were conducted to increase the compatibility of the MWNTs in the PA layer by grafting with abundant hydrophilic groups [11]. A significant water flux improvement was obtained without forfeiting the solute rejection. Besides, the particle size offers an additional degree of freedom to tailor the membrane permeability, selectivity, structure, morphology as well as the interface of TFN membranes [26]. Undoubtedly, the emergence of nanotechnology provides an attractive and facial alternative to improve membrane performance [27]. However, most TFN membranes showed a significant enhancement in water permeability at the expense of marginal decrease or maintained selectivity as summarized above. Particle size determines a defect-free membrane performance as observed by Mary L. Lind [26]. Larger sized particles especially impermeable inorganic nanoparticles easily produce non-selective voids formed between the layers of the PA skin [18]. Smaller sized nanoparticles produce greater enhancements in membrane permeability and salt rejection [26]. Therefore, incorporation of more polymer compatible and smaller dimension nano-materials is an ongoing research prospect for improving PA TFN membrane desalination performances.

As an emerging class of carbonaceous nanomaterials, carbon dots (CDs) have drawn tremendous attention since its first synthesis in 2004 [28]. Due to their low toxicity, excellent water dispersibility, ease of synthesis and functionalization as well as their photo stability, they are have been explored intensively for their potential application in bioimaging, biosensing and other biological related fields [29–31]. Carbon dots are luminescent nanoparticles with nanosize generally less than 10 nm, and can be produced in large-scale through a wide range of carbon sources using inexpensive facial approaches [30,32]. The size and surface properties of CDs nanoparticles can be easily tuned by changing the raw material or reaction parameters [33,34]. The amount of functional groups on the carbon dots such as carboxyl, carbonyl, hydroxyl, amino and other oxygenous groups makes it highly soluble and biocompatible [29,31]. For this reason, incorporation of CDs into polymeric membrane may be a plausible approach. Carbonaceous materials, such as CDs have high affinity for polyamide materials, therefore hydrophilic CDs not only can be utilized to enhance the hydrophilicity of membrane surface but also to tailor the morphology, roughness, thickness and density of polyamide structure. Consequently, these unique properties and advantages make CDs a promising material for TFN reverse osmosis membrane modification.

To our knowledge, there is no report about the incorporation of carbon dots into polyamide TFC membrane. Herein, a super hydrophilic carbon dots with nanosize of 6.8 nm applied as nanofiller in TFN membranes for improved water desalination. In this paper, we utilize this special class of carbon material, which is also an environmental friendly nanoparticle to structurally modify the selective layer of the polyamide membrane to improve the flux and enhance/stabilize the membrane selectivity. We hypothesized that the abundant hydrophilic functional groups on the CDs could 1) enhanced the solubility and diffusivity of MPD molecules during interfacial polymerization producing a slightly dense PA interface, which speculatively may be as a result of the slight increase in interfacial tension and solubility difference and thus, provides an important implication for solute selectivity of the novel nano-enhanced membrane; 2) create an intrinsic pathway to enhance the membrane permeability and also impact the salt rejection through repulsive charge production; and 3) increase the roughness of the surface morphology thereby expanding the wettability of the outermost support layer. The effects of CDs loading concentrations and deposition time on the membrane separation performance were also investigated.

2. Experiments

2.1. Materials and reagents

The microporous polysulfone support (PSf) with nonwoven polyester fabric was fabricated in the lab through phase inversion. The active polyamide layer of the RO membrane was formed by interfacial polymerization of monomers of m-phenylenediamine (MPD, 99%, Sigma- Aldrich) in aqueous phase and trimesoyl chloride (TMC, 98%, Sigma- Aldrich) in organic phase reaction. Besides, chemicals in aqueous phase included triethylamine (TEA, 99.5 + %, Sigma-Aldrich), (+)-10-camphorsulfonic acid (CSA, 99%, Sigma- Aldrich) and Isopar G® (ExxonMobil Chemical) used as solvent in organic phase. Raw materials used for the synthesis of the Carbon-dots included D-(+)-Glucose anhydrous ($C_6H_{12}O_6$, > 99.7%, Sinopharm Chemical Reagent Co., Ltd), Potassium dihydrogen phosphate (KH_2PO_4, > 99.7%, Sinopharm Chemical Reagent Co., Ltd) and ethanol (C_2H_6O, > 99.7%, Sinopharm Chemical Reagent Co., Ltd), which was used for precipitation of free salt. The membrane permeability and rejection performance were tested using sodium chloride (NaCl, > 99.7%, Sinopharm Chemical Reagent Co., Ltd). All the chemicals were used as received. Deionized (DI) water was used throughout the experiments. The BW30 membrane was kindly provided by Dow Water & Process Solutions.

2.2. Synthesis of CDs

In this work, the hydrothermal treatment step using glucose as substrate is similar to that reported by Zheng et al. [35] and is as follows: 1.0g of glucose and 1090 mg of KH_2PO_4 were dissolved in 40 mL of deionized water. The solution mixture was transferred into a 100 mL Teflon-lined autoclave and purged with N_2 for 1 h to remove O_2 dissolved in the solution. After hydrothermal reaction in the oven at 473 K for 12 h, the resulting brown precipitates were recovered by centrifugation at 7830 rpm for 15 min and filtered through a 0.22 µm filter. The yellow supernatant was collected and freeze dried. The obtained fine milky powder was re-dispersed in ethanol through vortexing to precipitate the free salt. The yellow ethanol solution was further filtered through PTFE syringe filter with pore size of 0.22 µm and rotary evaporation was conducted to remove ethanol gently. The muciform CDs obtained were kept in dryer for further characterization and use. It should be noted that the obtained liquid-like CDs nanoparticles were sticky and therefore restricts the complete elimination of ethanol by the rotary evaporation process. This residual trace of ethanol bonded tightly together by hydrogen bond carries hydroxyl and carboxyl functional groups on the surface of CDs, which resulted in a dark brown dope (Fig. 1).

2.3. Preparation of CDs -TFN RO membrane

The CDs-TFN RO membrane was fabricated by interfacial polymerization on the PSf membrane. The support PSf membrane was cut and