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Impact of nanoparticles surface characteristics on pore structure and performance of forward osmosis membranes

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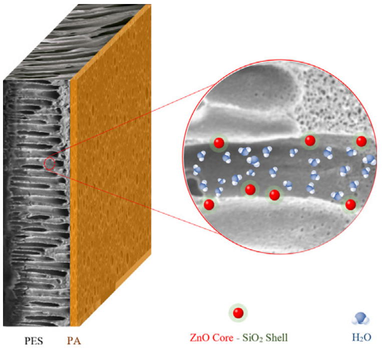
HIGHLIGHTS

- A versatile method is used to synthetize core-shell ZnO-SiO_2 nanoparticles.
- Capping effect of SiO_2 shell is used to impede ZnO core expansion.
- Synthesized nanoparticles are employed to modify FO membrane pore structure.
- Improved membrane performance is obtained when threated by ZnO-SiO_2 nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

Forward osmosis is a new emerging technology which has shown great potential in low cost and highly efficient water desalination. The major obstacle in further development of forward osmosis processes is internal concentration polarization which can significantly lower the water flux through the membranes. Herein, in order to increase the membrane hydrophilicity and thus, reduce the internal concentration polarization, polyethersulfone was selected as an efficient support layer and treated with nanoparticles of different surface characteristics. To fabricate such modified membranes, ZnO and stable ZnO-SiO_2 core-shell nanoparticles were dispersed within the polyethersulfone solution and subsequently, a thin active layer of polyamide was deposited on the obtained support layers by using interfacial polymerization method. Morphological characterizations revealed the major impact that nanoparticles surface properties had on cross-section pores structure which were formed within polyethersulfone support layers. The sponge like pores within the membrane support layers were changed from loose to long finger like structures when the polyethersulfone was chemically modified by ZnO and ZnO-SiO_2 core-shell nanoparticles, respectively. Moreover, permeate flux enhancements as high as 117% were observed in the membranes modified by ZnO-SiO_2 core-shell nanoparticles. This implied that such nanoparticles could be a promising candidate to improve the performance of forward osmosis membranes.

1. Introduction

Demands for safe and sustainable water resources have been paralleled by population growth and have been continuously increased

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during the last decades. Currently, about one-third of the world's population lives in countries that are suffering from water scarcity and it is expected that, by 2025, this estimate doubles [1,2]. Even though >70% of the Earth is covered in water, saline resources account for almost 97% of it and thus, cannot be used without being processed. Accordingly, preservation of existing freshwater and desalination of such abundant saline water resources should be considered seriously to cope with water stress challenges. In this regard, membrane based water desalination technologies with their unique advantages are believed to be able to address current and future water shortage issues [3]. Among the membrane technologies, reverse osmosis (RO) is one of the most ubiquitous methods used in water desalination. However, RO processes are relatively energy intensive and involve some practical problems, the most evident being high hydraulic pressures required to force water pass through the semi-permeable membranes. The energy consumption can even be increased during such processes as the RO membranes are prone to scaling and fouling [4]. Therefore, although in the last few decades significant efforts have been made to improve RO membrane performance, future application of such processes are still in doubt [5].

Forward osmosis (FO), on the other hand, as a new emerging technology and an alternative to pressure-driven membrane processes such as RO, has recently attracted remarkable interests due to its potentials in addressing water and energy scarcity problems [6]. In the absence of any external pressure, FO process utilizes naturally generated osmotic pressure difference across a semi-permeable membrane to spontaneously pull water out of a low concentrated feed solution to the draw solution of relatively higher concentration [7,8]. Thus, in theory, in contrast to the pressure–driven processes, no additional hydraulic pressure is required in FO process. Therefore, low operating cost and energy consumption, as well as minimal fouling and operating pressure, have made FO an economic alternative for pressure-driven membrane processes [6]. However, following the FO process, diluted draw solution should be recovered by using energy consuming separation processes such as RO or nanofiltration [6], and such expenses should also be considered to estimate the overall operating costs. Therefore, by using a properly designed FO process, not only the energy consumption can be reduced, but also the major practical problems associated with membrane fouling could be substantially avoided [9]. Accordingly, due to the numerous applications and the unique features it has, FO process has been studied extensively in different contexts such as desalination [10], wastewater treatment [11], food and pharmaceutical processing [12], agricultural fertilizing [13], and osmotic pressure power generation [14]. However, despite the recent advancements, finding a proper draw solution as well as internal concentration polarization (ICP) phenomena are still major bottlenecks that restrict widespread industrial applications of FO processes [15].

Identification of an appropriate draw solution is one of the major issues of FO processes. In general, low cost, low toxicity, minimal reverse solute flux, sufficiently high solute concentration (i.e. high osmotic pressure), and being easily recycled by a simple economic separation process are the most important characteristics of a proper draw solution [16]. Furthermore, ICP is another big challenge which should be well understood and considered throughout the FO processes. Over the past five decades, membrane technology has generally developed based on its applications in pressure-driven processes such as RO. In contrast to osmotically-driven processes like FO, mass transfer on the permeate side of the RO membranes is not a determining factor [17]. In FO membranes, mass transfer in both feed and draw sides play a crucial role in overall membrane performance. During FO, depending on the membrane orientation, two kinds of concentrative and dilutive ICPs can occur within the porous SL [9]. Due to the thick sponge-like structure of the highly tortuous support layer (SL), mass transfer would be restricted at the traverse boundaries of the porous SL. Therefore, ICP phenomenon may take place within the membrane SL, thereby leading to either concentration of the feed or dilution of the draw solutions in pressure retarded osmosis (PRO) mode (SL faces the feed solution), or FO (SL faces the draw solution) mode, respectively [17,18]. This implies that, to prevent severe ICP as much as possible, an ideal FO membrane should be as thin as possible, hydrophilic, and highly porous with small tortuosity [19]. So far, the huge amount of efforts have been made to synthesize FO membranes have resulted in some membranes of desired properties such as thin film composite (TFC) [20,21] and layer by layer (LBL) assembly membranes [22,23]. To design and optimize such membranes, while the salt rejection was kept intact, water flux through the membrane was maximized to lower the required process energy. Among these membranes, asymmetric TFC membranes have gained much consideration due to their superior separation performance over the wide range of temperature and pH [24]. The TFC membranes consist of polyamide (PA) as an active layer (AL) formed via interfacial polymerization (IP) on the surface of a porous SL.

To control the ICP in SL, different strategies have been proposed in literature. Among such various available techniques, chemical modification of SL by proper hydrophilic polymers or inorganic nanomaterials has been proven to be a practical method to lower the ICP by increasing the hydrophilicity of the interacting surfaces. It has been shown that the higher the hydrophilicity of the surfaces, the lower the fouling tendency would be, especially in the case of naturally hydrophobic foulants [25]. The SL tailored by hydrophilic polymers would be more prone to be drastically plasticized, thereby leading to AL delamination [26]. Furthermore, promising results have been obtained when the SLs were modified by some nanomaterials with specific structures, such as SiO_2 [27], TiO_2 [28], zeolite [29], multi-walled carbon nanotubes [30], halloysite nanotubes [31], and montmorillonite [20]. The PES surface has recently been coated with mineral $CaCO_3$ to increase FO membrane hydrophilicity [32]. Increased hydrophilicity of the SL significantly improves water flux while it has minimal impact on salt rejection rates. In another study, graphene oxide nanosheets have been used to modify FO membrane characteristics [33] and its optimal concentration to improve the membrane performance has been evaluated. Some researchers have also studied the role of membrane SL properties in the formation of PA top layer. Singh et al. have investigated the effect of pore sizes within the SL on salt rejection [34]. They found significant reduction in salt rejection efficiency when the average pore size of the membranes was increased from 0.07 to 0.15 μm. The influence of SL pore size on the PA formation was found to be responsible for such observations. Moreover, in another systematic research conducted on the TFC membrane in FO process [35], Huang et al. demonstrated that the smaller pore size in SL could result in denser formation of PA and subsequently, leading to better separation performance and higher pressure tolerance. Recent studies have also indicated the major influence that average pore radius of the SL can have on the overall performance of FO membranes [36]. Therefore, not only thickness, tortuosity, and porosity, but also other important parameters such as size and shape of the pores within the SL should be considered to improve membrane efficiency. However, although the overall performance of the membranes has shown to be influenced by the SL pore structure, the impact that embedded nanomaterials can have on such SL characteristics have not been well studied. Here, in this study, the impacts that nanoparticles surface characteristics had on the FO membrane SL pore structure were assessed. The FO performance of the membranes modified by ZnO and ZnO-SiO_2 core-shell nanoparticles were also investigated and compared with each other to verify how the surface properties affect the membrane hydrophilicity, porosity, and pore structure. To the best of our knowledge, no conclusive research has yet been published on the effect of core-shell nanoparticles in FO membrane desalination.

2. Materials and methods

2.1. Materials

Polyethersulfone (PES) (molecular weight: 58,000, Ultrason® E 6020, BASF Co, Germany), polyethylene glycol 200 (PEG-200) (Merck,

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