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Thin film composite membranes containing intrinsic CD cavities in the selective layer

Shu Xiong[a,b], Dong Yan Zhang[c], Shuang Mei[a], Jie Liu[c,*], Yu Sheng Shi[c], Yan Wang[a,b,d,**]

[a] Key Laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, Wuhan 430074, China
[b] Shenzhen Institute of Huazhong University of Science & Technology, Shenzhen 518000, China
[c] State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan, China
[d] Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science & Technology, Wuhan 430074, China

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ABSTRACT

In this work, β-cyclodextrin functionalized with multiple ethylenediamine groups (β-CD-EDA) is synthesized and employed as a novel amine monomer for the preparation of thin film composite (TFC) membrane via the interfacial polymerization (IP) with trimesoyl chloride (TMC), to incorporate uniformly-distributed intrinsic CD cavities into the polymer network of the selective layer. The chemical structure of the synthesized β-CD-EDA is confirmed by HMRS, FTIR, TGA XPS and ^{1}H NMR. The chemical properties, surface morphology and the separation performance of TFC membranes prepared with β-CD (TFC_β-CD) and β-CD-EDA (TFC_β-CD-EDA) as aqueous monomers are investigated and compared. The effects of the IP time and β-CD-EDA concentration on the membrane properties are investigated to optimize the membrane performance. The separation performances of TFC_β-CD-EDA membrane are further evaluated with feed solutions containing different solutes. It is found that TFC_β-CD-EDA membranes demonstrated competitive water permeabilities and high rejections to common divalent anionic salts and small organics, contributed by the CD cavities that enable the fast transport of water molecules but restrict larger ions or molecules. Besides, excellent fouling resistance of TFC_β-CD-EDA membrane is also found, because of the embedded CD rings with plentiful hydroxyls. This work is therefore believed to provide a facile method for the development of high-performance TFC membrane with pore-containing selective layer.

1. Introduction

Thin film composite (TFC) membranes have been widely applied in various membrane processes, particularly in water treatment processes, such as reverse osmosis (RO), nanofiltration (NF) and forward osmosis (FO), because of the facile membrane fabrication and the superior separation performance [1]. A typical TFC membrane is composed of a thin selective layer formed by the interfacial polymerization (IP) of active monomers in two immiscible phases and a porous substrate. The composite structure of the TFC membrane allows the convenient optimization of the thin selective layer and porous substrate independently, so that TFC membranes with different properties and performances can be facilely obtained. In past decades, great research interests have been devoted in the fabrication of novel TFC membranes with the optimized membrane performance, including improved membrane permeability, higher selectivity as well as greater resistance against chlorine, solvent, fouling, etc. [2,3].

Since the separation performances of the TFC membrane are mainly determined by the selective layer, the monomers and additives involved in the IP process will greatly affect the resultant TFC membrane performance. [4–6] By choosing monomers or additives with different chemical structures or properties, the surface properties and the membrane performance can be tuned facilely. For example, monomers containing hydrophilic groups [7,8] can be employed to prepare hydrophilic TFC membranes with the higher water flux and better fouling resistance; fluorine monomers [9,10] can be utilized to fabricate the TFC membrane with a better solvent tolerance; anti-bacterial TFC membranes can also be prepared with monomers containing anti-

* Corresponding author. State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan, China (Prof. Jie Liu)
** Corresponding author. Key Laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, Wuhan 430074, China. (Prof. Yan Wang)
E-mail addresses: hustliuj@hust.edu.cn (J. Liu), wangyan@hust.edu.cn (Y. Wang).

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Nomenclature

R_s	solute rejection	A	water permeability
C_f	feed concentration	ΔP	trans-membrane pressure
C_p	permeate concentration	A_m	membrane area
M_w	molecular weight	V	volume of permeate solution
		Δt	time interval

bacterial groups; [11] monomers with the bulky structure [12–14] may also contribute to the larger fractional free volume of the selective layer and therefore enhance the membrane permeability. In addition, inorganic salts, [15] surfactants [16] and nanoparticles [17–19] can also be incorporated in monomer solutions to regulate membrane properties. Among them, pore-containing nanoparticles are very attractive because of their permeable and selective channel provided by the pores, and exhibit great potentials to overcome the permeability-selectivity trade-off and achieve more significant enhancement in the membrane permeability. For example, TFC membranes with inclusion of pore-containing nanoparticles such as metal−organic frameworks (MOFs) [20,21], polyhedral oligomeric silsequioxanes (POSS) [22], and covalent organic frameworks (COFs) [23] show significantly improved permeability and well-maintained selectivity, ascribed to the high porosity and the good affinity to the polymer matrix of these nanoparticles. Nevertheless, unsatisfactory dispersion and thorny agglomeration of these nanoparticles at higher loadings still exist, which hinders the application of nanoparticle in the TFC membrane preparation.

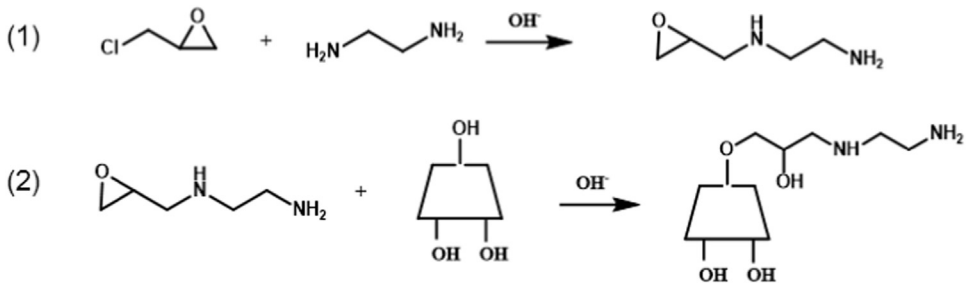
The convenience of regulating membrane properties by the monomer selection and the merit of incorporating pore-containing nanoparticles inspire us to seek for a pore-containing monomer for TFC membrane fabrication, in order to achieve both competitive permeability and selectivity as compared to those prepared with the ordinary monomers, and to avoid the ineluctable agglomeration of the pore-containing nanoparticles. In this work, therefore, a pore-containing compound, β-cyclodextrin functionalized with multi-ethylenediamine groups (β-CD-EDA), is employed in IP as the aqueous monomer to fabricate a novel TFC membrane with intrinsic rigid pores embedded in the selective layer. CD, a cyclic oligosaccharide consisting of 6–12 glucose units with the subnano-scaled intramolecular cavity and abundant hydrophilic hydroxyl groups in the cavity exterior, has long been used in the membrane preparation for pervaporation [24,25], gas separation [26–28] and enantioseparation [29] due to their suitable pore size, sieve exclusion effect, molecular cognition capacity, and easy availability. However, few studies [30–32] have explored the application of CD in the fabrication of TFC membranes so far. It has been reported that the TFC membrane prepared with the addition of β-CD in the aqueous monomer showed an improved hydrophilicity and a higher water permeability, contributed by the rich hydroxyl groups and additional water passage of the CD cavity [30]. However, the membrane selectivity declined with increasing β-CD concentration and CD agglomeration beyond a threshold loading, due to the low reactivity and poor solubility of β-CD in water. Amine-functionalized CDs were also reported to in-suit modify TFC membrane by forming amide bond with the formed PA network and improve the membrane water permeability without the rejection decline [31,32].

To maximize the advantages of the well-defined CD cavity in the promotion of TFC membrane performance, a novel amine modification strategy of β-CD is employed in this work to endow β-CD with multiple functional ethylenediamine groups, so it can be used as the aqueous monomer alone for the preparation of novel TFC membranes by IP. By the polymerization of β-CD-EDA and the organic monomer acyl chloride, the as-formed selective layer contains uniformly-distributed intrinsic CD cavities in the polyamide network, and possesses the good hydrophilicity rendered by plentiful hydroxyls in CD. Desirable high permeability and selectivity of the TFC membrane is therefore expected. Ethylenediamine-substituted β-CD is synthesized by a facile method and characterized with various techniques such as HMRS, FTIR, NMR, XPS and TGA. TFC membranes prepared with pristine β-CD and β-CD-EDA are studied and compared to explore the feasibility of β-CD-EDA as an aqueous monomer for the TFC membrane preparation. The effects of IP conditions (β-CD-EDA concentration and IP time) are also investigated to optimize the membrane physicochemical properties and the separation performance for different solutes and the waste water treatment. This work is believed to shed valuable insights to the development of high-performance TFC membranes for future separation applications.

2. Experimental and materials

2.1. Reagents and materials

β-CD, TMC, humic acid (HA) and sodium alginate (SA) were purchased from Aladdin Chemical Reagent Co. Ltd. Ethylenediamine (EDA), potassium hydroxide (KOH), sodium hydroxide (NaOH), hydrochloric acid (HCl, 36–38%), inorganic salts (LiCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$), organic salts (sodium gluconate (Glu-Na)), trisodium citrate (CA-3Na) and ethanol were all provided by Sinophatm Chemical Reagent Co. Ltd. Epichlorohydrin (ECH) and triethylamine (TEA) were obtained from Shanghai Linfeng Chemical Reagent Co. Ltd. Polyacrylonitrile (PAN) with a molecular weight of 250 kDa was purchased from Hubei Chushengwei Corporation. N-dimethylformamide (DMF) and n-hexane were supplied from Tianjin Enox Chemical Reagent Co. Ltd. and Tianjin Fulu Fine Chemical Co., Ltd., respectively. Bovine serum albumin (BSA) was provided by Shanghai Yuanye Bio-Technology Co., Ltd. All above chemicals were of reagent grades. Deionized (DI) water was generated in laboratory by a Wuhan Pin Guan Ultrapure LAB system.



Scheme 1. Synthesis route of β-CD-EDA.