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Nanocomposite organic solvent nanofiltration membranes by a highly-efficient mussel-inspired co-deposition strategy

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ABSTRACT

Herein, a novel nanocomposite organic solvent nanofiltration (OSN) membrane has been facilely fabricated by a highly-efficient one-step co-deposition of mussel-inspired catechol and octaammonium polyhedral oligomeric silsesquioxane (POSS-NH$_3^+$Cl$^-$) onto supports. The basic properties and morphologies of the co-deposited nanocomposite membranes were investigated with various physicochemical characterizations in detail. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra proved the present of POSS nanoparticles on membrane surface. X-ray photoelectron (XPS) results suggested the optimal ratio of POSS-NH$_3^+$Cl$^-$ and catechol for co-deposition. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images demonstrated the formation of a layer on support surface. The optimized nanocomposite membrane exhibited an ethanol (EtOH) permeance of 1.26 L m^{-2} h^{-1} bar^{-1} with a rejection of 99% to Rose Bengal (RB). The novel membrane also exhibited remarkable separation performance for dyes removal from a wide range of solvents including challenging polar aprotic and strongly swelling solvents. Particularly, the nanocomposite membrane demonstrated stable performances during a two-day long term test in DMF for RB concentration. In addition to providing a highly-efficient way to high-performance OSN membrane, this work may stimulate the bio-inspired design of advanced nanocomposite membranes for environmental applications.

1. Introduction

Organic solvent nanofiltration (OSN) is a relatively new technology that allows efficient and sustainable separation of molecules with molecular weights between 200–1000 g mol^{-1} from organic solvents as well as solvent recovery by simply applying a pressure gradient across a membrane [1]. It has the merits of low energy consumption, environmental friendliness and safety comparing to the conventional separation technologies such as crystallisation, extraction and chromatography [2,3]. The development of OSN membranes with high stability in a wide range of solvents and good separation performance is still a challenge and has attracted increasing attention. In recent years, nanocomposite membranes with nanoparticles incorporated in polymer matrix have shown great promise in OSN application. These membranes combine the advantages of polymer membranes (proces-

sability, flexibility, inexpensive) with the unique features of inorganic nanoparticles (porosity, hydrophobicity/hydrophilicity). Compared with their reference materials, the nanocomposite membranes usually show higher permeance and/or selectivity [4,5].

So far, most of the reported nanocomposite OSN membranes are thin film nanocomposite (TFN) membranes, in which nanoparticles have been embedded into the active layer on top of a support to improve membrane performance. A diversity of nanoparticles including MOFs [6], silicalite [7], TiO$_2$[8], SiO$_2$[8] and SWCNTs [9] etc. have been deployed for TFN OSN membrane fabrication via interfacial polymerization or direct coating method. Despite of the improved membrane performance, these methodologies still suffer some drawbacks. Interfacial polymerization generally involves three steps besides pretreatment and posttreatment. First, the selective surface of support is contacted with an aqueous solution consisting of amine monomer.

Second, the excess of aqueous solution on surface is moved. Third, the surface is contacted with second organic solution containing trimesoyl choride [10]. The operation time of each step ranges from seconds to minutes, coupled with the poor dispersion of nanoparticles in aqueous or organic phase, makes it hard to obtain a repeatable membrane performance. For direct coating approach, the use of viscous coating solution typically yields separation layer with thickness up to tens of micrometers, which subsequently results in the great decline of solvent permeance [11].

The mussel-inspired polydopamine coating method has attracted considerable interest these years. Under a weak alkaline aqueous solution, dopamine can spontaneously oxidize and self-polymerize to form polydopamine [12]. This self-polymerization reaction concurrently occurs both at any pre-immersed substrate surface to form deposition and in solution to form aggregation [13,14]. It has been widely used as a universal and versatile tool in material surface engineering for various applications, although the exact polymerization and interaction mechanism of the adhesive polydopamine layer was still unknown so far [15]. Specially, polydopamine modified membranes have been used as substrates, while dopamine have been employed as aqueous phase monomer in interfacial polymerization to prepare OSN membranes [16,17]. It is commonly acknowledged that the catechol and amine groups in dopamine structure are critical factors during the process of dopamine self-polymerization, and a system containing catechol and amine groups could replace dopamine and co-deposited on various substrates by simulating a similar polymerization mechanism [12]. This could potentially broaden the molecular diversity of dopamine and its derivatives. Co-deposition of catechol and well-designed functional molecules could provide great potential for target functional materials and coatings. Nevertheless, currently there are still few research works on this issue [18,19]. Very recently, our group has reported a composite NF membrane via the co-deposition of catechol and branched polyethylenimine for textile wastewater treatment [20]. To the best of our knowledge, the co-deposition of catechol with nanoparticle has not been reported.

Herein, for the first time, we reported the facile one-step co-deposition of catechol and octaammonium polyhedral oligomeric silsesquioxane ($[SiO_{1.5}(C_3H_6NH_3^+Cl^-)]_8$, referred to as POSS-$NH_3^+Cl^-$) onto cross-linked polyimide supports to fabrication nanocomposite OSN membranes, as shown in Fig. 1. Polyhedral oligomeric silsesquioxane (POSS), which possesses a siloxane cubic core framework with a 0.53 nm pore size and a spherical diameter of 1−3 nm

[21], has previously been incorporated into membranes for gas separation [22] and water treatment [23]. POSS-$NH_3^+Cl^-$ was used in this study because the amine groups at arms of POSS-$NH_3^+Cl^-$ can ensure high cross-linking density and endows the resulting nanocomposite membrane with good solvent resistance. The possible polymerization mechanism behind co-deposition has been explored. The morphologies and physicochemical properties of the as-prepared composite membrane were regulated by the mass ratio of POSS-$NH_3^+Cl^-$/catechol. The separation performance toward dyes in a widely range of solvents, long term operation performances and mechanical properties of the composite membrane were investigated in detail.

2. Experimental

2.1. Materials

A polyimide (PI) polymer, P84®, was provided by Granulat SG STD. Tris (hydroxymethyl) aminomethane (Tris), 1,6-hexanediamine (HDA), catechol, Methyl Orange (MO), Rose Bengal (RB), Crystal Violet (CV), Orange G (OG), Acid Fuchsin (AF), Methyl Blue (MB) and Solvent Blue II (SB II) were obtained from Aladdin Industrial Co., Ltd. Octaammonium POSS (POSS-$NH_3^+Cl^-$) was purchased from Hybrid Plastics Inc. All organic solvents were supplied by Xilong Chemical Industrial Co., Ltd. All used water was deionized.

2.2. Membrane preparations

2.2.1. Preparation of PI support

A P84 UF membrane was fabricated by a traditional non-solvent induced phase separation process. Prior to use, the polymer was first dried in a vacuum oven at 120 °C overnight to remove moisture. A polymer solution was prepared by dissolving 15 wt% of P84 in NMP and stirring until complete dissolution. The solution was allowed to stand for a further 12 h at room temperature to remove any trapped air bubble and then cast on a glass plate using a casting knife set to a thickness of 200 μm. The polymer membranes were then precipitated from solution via immersion in water. The membranes were then immersed in IPA to remove water from the polymer matrix, and then transferred to a 20 g L^{-1} solution of HDA in IPA overnight for crosslinking. Next, the membranes were washed with IPA to remove any residual HDA and then stored in fresh IPA before use.
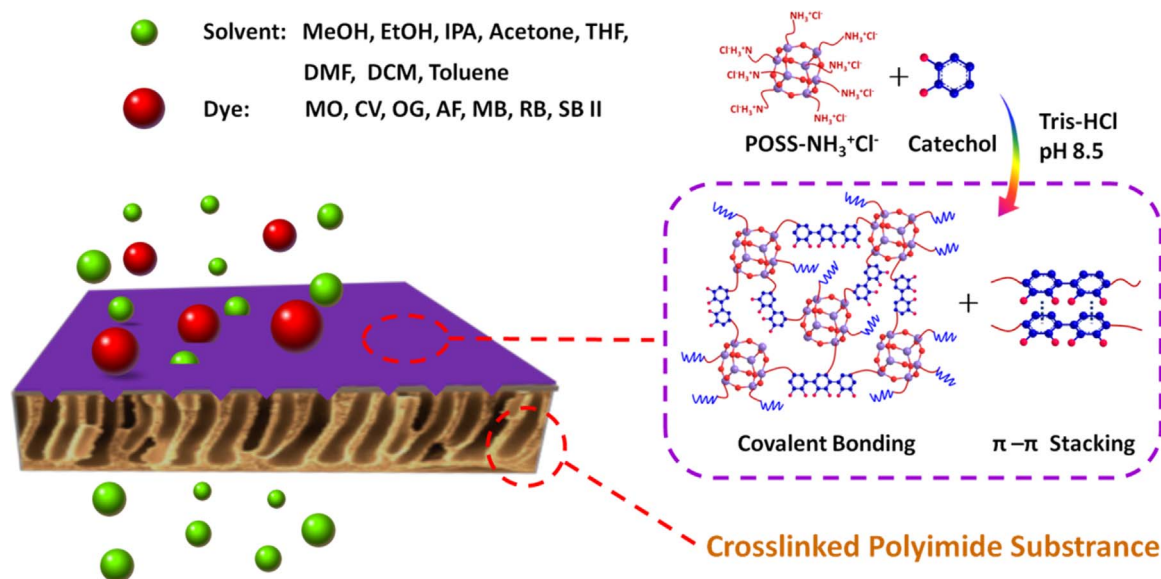

Fig. 1. Schematic illustration of the fabrication of novel nanocomposite NF membranes via the mussel-inspired co-deposition of catechol and POSS-$NH_3^+Cl^-$ for organic solvent nanofiltration.