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\textsubscript{3}+CT) 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\textsubscript{3}+CT 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\textsuperscript{-2} h\textsuperscript{-1} bar\textsuperscript{-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\textsuperscript{-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 (processability, 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\textsubscript{2} [8], SiO\textsubscript{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. After some drying and/or pretreatment and posttreatment, the selective surface of support is contacted with an aqueous solution consisting of amine monomer. After some drying, the selective surface of support is contacted with an aqueous solution consisting of amine monomer. After some drying, the selective surface of support is contacted with an aqueous solution consisting of amine monomer. After some drying, the selective surface of support is contacted with an aqueous solution consisting of amine monomer. After some drying, 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 trimesoxy chloride [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 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 (POSS-NH$_3$$^+$Cl$^-$) onto cross-linked polyimide for fabrication nano-composite OSN membranes, as shown in Fig. 1. Polyhedral oligomeric silsesquioxane (POSS), which possesses a siloxane cubic core framework with a 0.53 nm pore size and a spherical diameter of 1–3 nm [21], has previously been incorporated into membranes for gas separation [22] and water treatment [23]. POSS-NH$_3$$^+$Cl$^-$ 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, 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, 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 cross-linking. 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.](image-url)
2.2. Preparation of co-deposited nanocomposite membranes

The co-deposited membranes were facilely fabricated by a one-step co-deposition of catechol and POSS-NH$_3^+$Cl$^-$ onto the PI substrates. First, catechol (100 mg) and POSS-NH$_3^+$Cl$^-$ with determined mass ratios were dissolved in a Tris-HCl buffer solution (100 mL, pH 8.5). Subsequently, the PI substrates (5 cm×5 cm) were immersed in the above solutions and shaked at 30 °C for 0.5–3.5 h. Then, the modified membrane was rinsed with DI water for several times to remove unreacted residuals. The clean nanocomposite membrane was stored in DI water for further use.

2.3. Membrane characterizations

The ultraviolet-visible (UV–vis) absorption of the centrifuged clear coating solution was measured with an ultraviolet spectrophotometer UV 2450 (SHIMADZU, Japan). The chemical structure of the function layer was characterized by Fourier transform infrared spectroscopy (FT-IR, Perkin-Elmer, USA) and X-ray photoelectron spectra (XPS, AXIS UltraDLD, SHIMADZU, Japan). The water contact angles of membranes were measured by a contact angle measuring system (G10 Kruss, Germany). At least five values at different sites were attained to calculate an average. The morphologies of the membranes were characterized by scanning electron microscopy (SEM, Hitachi SU8000). Element composition of the functional layer was concurrently analyzed by Energy-dispersive X-ray spectroscopy (EDX) on the same equipment. Surface roughness of the membranes was observed by atomic force microscopy (AFM, Nanoscope IIIa) in air atmosphere. Mechanical strength of the membranes (50 mm×15 mm×0.13 mm) was evaluated on an AG-1 Universal Tester (SHIMADZU, Japan) at a strain rate of 5 mm min$^{-1}$. Five membranes of each type were tested to calculate the average value.

2.4. Membrane performance evaluation

All filtration experiments were carried out at 5 bar using a self-made dead-end stirred-cell filtration apparatus (Fig. A1). The effective membrane area was 21.2 cm$^2$ and at least three independently prepared membranes were tested. The membranes were conditioned for 2 h at 5 bar to reach a steady value before permeance and rejection measurements. Solutions of dyes (35 μmol L$^{-1}$) in a variety of solvents were used as feeds. The feed was stirred at 700 rpm in the cell to minimize concentration polarization. The membrane permeance was measured as given in Eq. (1):

$$P = \frac{V}{A \times t \times \Delta P}$$

where P is the permeance (L m$^{-2}$ h$^{-1}$ bar$^{-1}$), V (L) is the volume of permeate in an operating time t (h), A is the effective area (m$^2$) and ΔP is the applied pressure across the membrane (bar).

The rejection of dyes was calculated from Eq. (2):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\%$$

where $C_p$ and $C_f$ were the dye concentrations in the permeate and the feed, respectively. Dye concentrations were measured by a UV–vis Cintra20-GBC apparatus.

3. Results and discussion

3.1. Reactive behaviour in coating solution and possible mechanism

Optical images of coating solutions with different POSS-NH$_3^+$Cl$^-$/catechol mass ratio after 2.5 h was shown in Fig. 2(A). The coating solution with sole catechol was light-colored, while it gradually turned dark brown as a function of POSS-NH$_3^+$Cl$^-$/catechol mass ratio from 1:1 to 10:1. The reactions between the two parties were revealed by UV–vis spectroscopy. As a control, the curves of the sole catechol (at neutral pH) and POSS-NH$_3^+$Cl$^-$ (at pH 8.5) solutions were also presented. Fig. 2(B) shows that the solution with sole catechol at neutral pH exhibits one significant absorption peak at 275 nm. The presence of a new absorption peak at 330 nm at pH 8.5 may be due to the oxidation of catechol into o-quinone. This reaction is similar to the oxidation of dopamine (270 nm peak) into dopaquinone (350 nm peak) during dopamine self-polymerization [24]. The intensity of this peak was magnified with the increase of POSS-NH$_3^+$Cl$^-$/catechol mass ratio, indicating that amine group of POSS particle could accelerate the oxidation of catechol [25]. Meanwhile, the peak at 275 nm broadened, which is probably an evidence of cross-linking of quinone into phenol-coupled oligomers [26]. It should be noted that an absorption peak at about 480 nm is generally reported for dopamine coating solution and related to the intramolecular cyclization and subsequent oxidation reactions during polymerization [24]. However, this peak was not observed in Fig. 2(B), which is probably due to the fact that the intrinsic isolation nature between catechol and amine group has ruled out the possibility of intramolecular cyclization in our system [18].

Quite interestingly, some aggregates can be observed in the coating solution with a POSS-NH$_3^+$Cl$^-$/catechol mass ratio of 5:1, whereas no visible aggregates can be found in solutions with 0:1, 1:1 and 10:1 (Fig. 2(A)). Comparing to sole catechol coating (0:1), the prime amine group in co-deposited solution can facilitate the formation of aggregates by contributing to the extra cation-π interactions (e.g. NH$_3^+$-quinone/benzene/phenol) [27]. At a relatively lower POSS-NH$_3^+$Cl$^-$/catechol mass ratio, such as 1:1, the aggregation rate in solution could at a low level due to the large mean free path between POSS-catechol intermediates. With increasing the POSS-NH$_3^+$Cl$^-$/catechol mass ratio, the concentration of POSS-catechol intermediates increased and the mean free path between them reduced, which substantially promoted the aggregation rate in solution. Thus, some visible aggregates precipitated when the POSS-NH$_3^+$Cl$^-$/catechol mass ratio increased to 5:1. However, further increase in mass ratio of POSS-NH$_3^+$Cl$^-$/catechol to 10:1 would result in the excess of amine groups in solution, which would disturb the non-covalent interactions between POSS-catechol intermediates and inhibit the formation of aggregates [28,29].

The aggregates were collected, washed with DI water and characterized by FT-IR and XPS in order to identify their chemical structure. As shown in Fig. 3(A), in the curve of catechol, the peaks at 3450 and 3325 cm$^{-1}$ are assigned to -OH, and the multiple peaks in the range of 1630–1700 cm$^{-1}$ are related to aromatic ring frame vibration. In the spectrum of POSS-NH$_3^+$Cl$^-$, the peaks located at 2950 and 1110 cm$^{-1}$ are related to ammonium salt stretching vibration and Si-O-Si asymmetric vibration in POSS cage, respectively [30,31]. Compared with POSS-NH$_3^+$Cl$^-$, the spectrum of aggregates show not only the peak assigned to Si-O-Si group in POSS cage but also aromatic ring characteristic peaks related to catechol. In addition, the peaks related to -CH$_2^-$ and -OH/-NH- can also be observed in the curve of aggregates. No discernable peak assigned to carbonyl group can be observed, which could be due to the absorbance was obscured by the broad peak centered at 1580 cm$^{-1}$[32]. Therefore, the FT-IR results demonstrate that the cross-linking reaction between POSS-NH$_3^+$Cl$^-$ and catechol.

The XPS spectrum of the aggregates in Fig. 3(B) exhibits C, N, O and Si peaks simultaneously, further confirming the formation of hybrid aggregations. It should be pointed out that the sole POSS-NH$_3^+$Cl$^-$ did not lead to any aggregate. The N 1 s spectra of aggregates were fitted with two peaks assigned to C-NH$_3^+$ at 401.3 eV and -C-NH at 399.2 eV (Fig. 3(C)). The major contribution to N 1 s came from -C-NH, inferring the Michael addition reaction during polymerization. The absence of Cl peak in the spectra suggests ammonium chloride salt did not existed in the aggregates. The possible production of C-NH$_3^+$ could be ascribed to spontaneous proton transfer from the acid (catechol, C-OH) to the amine (C-NH$_2$) [14]. The ratio of the intensities of the two N
1 s peaks indicates that about 6 of the 8 functional groups of the POSS molecule are involved in the Michael addition reaction. It is intriguing to find that the peak at a lower binding energy, which was generally reported in N 1 s spectra of polydopamine due to the intramolecular cyclization and subsequent oxidization reactions [14], was not been observed in this study, further confirming the conclusion from UV–vis measurements. In addition, analyses of C 1 s, O 1 s and Si 2 s (Fig. A2) also proved the existence of quinone and the formation of catechol-POSS complex.

As a result, we proposed a possible polymerization mechanism of POSS-NH$_3^+$Cl$^-$ and catechol, as shown in Fig. 4. In an alkaline solution, catechol was oxidized to quinoid form [24]. Meanwhile, the ammonium chloride groups in POSS-NH$_3^+$Cl$^-$ were deprotonated to form primary amines, which subsequently reacted with quinoid via Michael addition.

![Fig. 2.](image)

Fig. 2. (A) Optical images and (B) UV–vis spectra of typical coating solutions.

![Fig. 3.](image)

Fig. 3. (A) FTIR spectra of catechol, aggregates and POSS-NH$_3^+$Cl$^-$, (B) XPS spectra and (C) N 1 s spectra of aggregates.
reaction to yield an enedione structure. Subsequently, the cross-linking between quinoid and enedione via a reverse dismutation reaction resulted in phenol-coupled oligomers [26]. The covalent bonding in oligomers and the noncovalent bonding, such as π-π stacking, hydrogen bonding and charge transfer interactions, among oligomers contributed to the aggregate in solution or co-deposition on substrate [33]. Additionally, the intramolecular cyclization reaction did not happen in our system based on XPS and UV–vis analyses.

3.2. Chemical properties of nanocomposite membranes

The optical images of support and the co-deposited membranes show that the color of the membranes gradually changed from yellow to dark brown as the mass ratio of POSS-NH$_3$$^+$Cl-/catechol increased (Fig. A3), implying the possible formation of co-deposition on the membrane surfaces. The presence of POSS on the co-deposited membrane was confirmed by ATR-FTIR (Fig. 5). A new peak related to Si-O-Si group in POSS cage emerged at 1110 cm$^{-1}$ after co-deposition, indicating that the POSS structure has been successfully deposited onto cross-linked PI supports. Some other peaks observed in aggregates are undiscernable in the co-deposited membrane, which could be due to the few amount of co-deposition on membrane surface.

The XPS wide scanned spectra of the membranes are shown in Fig. 6(A). All the membrane shared three major peaks of C 1 s, N 1 s and O 1 s. Si 2 s and Si 2p peaks emerged with POSS-NH$_3$$^+$Cl- addition, and the Si atom concentration showed a maximum value for 5:1 scenario as shown in Table 1. The element ratios of C/Si, N/Si and O/Si in each co-deposited membrane also exhibited the same trends. In addition, Cl 1 s peak emerged when the mass ratio of POSS-NH$_3$$^+$Cl-/catechol increases to 6:1 and 10:1. Membrane relative weight gain also followed the same trend with that of the Si concentration (Fig. 6(B)), and 5:1 is probably the optimal ratio for the deposition on membrane surface, which is corresponding to the formation of aggregations in coating solutions. Moreover, the absence of aromatic N peak again in the N1s spectra of composite membranes, as shown in Fig. 6(C), further confirms that intramolecular cyclization did not occur during co-deposition process.
3.3. Morphologies, surface properties and mechanical properties of various membranes

Fig. 7 shows the morphologies of the PI support and the composite membranes. Nano-sized pores can be observed on the top surface of support and the one treated by sole catechol, suggesting that the deposition amount of polyphenol is not enough to completely cover the support top surface and it is unlikely to construct a dense coating by catechol alone [27]. Obviously, with the assistance of POSS-NH$_3^+$Cl$^-$, the nanopores vanished and a coating appeared on the membrane top surface due to the enhancement of prime amine on co-deposition process by introducing the extra cation-$\pi$ interactions [27]. When the mass ratio of POSS-NH$_3^+$Cl$^-$/catechol increased to 5:1, some nano-spheres emerged on membrane top surface, implying the improved co-deposition behaviour. Analogous nanospheres have also been observed in polydopamine modified substrates [24,34,35]. Further increasing POSS-NH$_3^+$Cl$^-$/catechol mass ratio to 10:1, although the co-deposition on support still occurred, the surface became relatively smoother due to the excessive amine groups suppressed the co-deposition process. The cross-sectional images of modified membranes showed no significant boundaries between support and coating layer. This can be explained by the following reasons: (1) catechol and POSS-NH$_3^+$Cl$^-$ molecules penetrated into the nanopores of supports and polymerized in the pores, obscuring the boundaries [29]; (2) the coating is too thin to be detected. The blurry boundary between support and coating layer has also been reported in some polydopamine modified substrates [29,36,37]. No appreciable morphological changes can be observed from the bottom surface and cross-section of membranes (Fig. A4). Optical image of the modified membrane shows that the top surface of membrane is significantly darker than the bottom surface (Fig. A5). These indicate that the co-deposition mainly occurred at the top surface of support.

AFM images show that the smooth surface of pristine support became rough after coating. The roughness of coated membranes exhibited a maximum value for the one with a POSS-NH$_3^+$Cl$^-$/catechol mass ratio of 5:1. Furthermore, EDX mapping reveals that C, N, O and Si were distributed homogenously on the membrane surfaces (Fig. A6), indicating the homogeneity of the hybrid coatings.

Fig. 6. (A) XPS spectra and (B) relatively weight gain of typical membranes, and (C) N 1s spectra of 5:1 co-deposited membrane.

<table>
<thead>
<tr>
<th>Membrane Composition (at%)</th>
<th>Atom ratio</th>
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<tbody>
<tr>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>Support 76.07 9.42 14.51 0 0</td>
<td>–</td>
</tr>
<tr>
<td>0:1 73.14 9.57 16.23 0 0</td>
<td>–</td>
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<tr>
<td>1:1 66.98 7.66 23.96 1.40 0 48.84 5.47 17.11 0</td>
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<tr>
<td>4:1 64.80 9.25 21.70 4.25 0 15.25 2.18 5.11 0</td>
<td></td>
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<tr>
<td>5:1 63.17 9.12 22.37 5.34 0 11.83 1.71 4.19 0</td>
<td></td>
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<tr>
<td>6:1 63.60 9.85 22.44 3.91 0.19 16.27 2.52 5.74 0.05</td>
<td></td>
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<tr>
<td>10:1 65.40 10.84 20.53 2.94 0.28 22.24 3.69 6.98 0.10</td>
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3.3. Morphologies, surface properties and mechanical properties of various membranes
surface, indicating the formation of a polymer layer on support [35,38,42]. Water contact angles of various membranes were demonstrated in Fig. 9. The crosslinked PI support showed a water contact angle of 58°, which is consistent with the previous reported results [43,44]. After deposited by catechol, the membrane water contact angle decreased to 50°, which could be related to the hydrophilic -OH group on membrane surface after deposition. With the addition of POSS-NH$_3^+$Cl, the water contact angle initially increased with POSS-NH$_3^+$Cl/catechol mass ratio ranging from 1:1 to 5:1, then decreased with POSS-NH$_3^+$Cl/catechol mass ratio ranging from 5:1 to 10:1. The initial increase of water contact angle could be due to the presence of hydrophobic POSS groups on surface and the increased surface roughness, although the remaining -NH$_3^+$ also affect the surface properties [45]. The decrease of water contact angle with further increasing catechol/POSS mass ratio could be rationally explained by the decrease in both co-deposition amount and surface roughness.

The mechanical strength of OSN membrane is a key factor to evaluate their usefulness in practical application [46,47]. It has been reported that the incorporation of POSS derivatives into polymer materials can dramatically improve polymer mechanical properties [48]. So we are intrigued if the membrane mechanical properties have also been improved after co-deposition. The tensile strength and breaking elongation of various membranes was shown in Fig. 10. It was obvious that sole catechol deposited membrane exhibited no significant different mechanical properties with PI support. While, both tensile strength and breaking elongation have increased after POSS-NH$_3^+$Cl addition, indicating the reinforcement effect of POSS nanoparticles. The tensile strength has increased from 3.22 to 4.77 MPa with almost 48% increase and the breaking elongation also improved from 1.95–4.04% with almost 107% improvement. The improvement of tensile strength and breaking elongation could be related to the covalent bond between POSS and polymer matrix, as well
as a certain degree of branched structure originated from POSS [49,50]. The highest breaking elongation at POSS-NH₃⁺Cl-/catechol mass ratio of 5:1 might be due to the highest co-deposition amount at this ratio.

3.4. Nanofiltration performance in organic solvent system

3.4.1. Effect of catechol/POSS mass ratio and coating time on separation performance

The organic solvent nanofiltration experiments of co-deposited membranes were carried out with a 35 μM RB solution in EtOH to evaluate the effect of POSS-NH₃⁺Cl-/catechol mass ratio on separation performance. The coating time was fixed at 2.5 h. As shown in Fig. 11(A), the sole catechol coated membrane (POSS-NH₃⁺Cl-/catechol mass ratio of 0:1) exhibited no obvious change in terms of both permeance and RB rejection, due to the limited coating efficiency as evidenced by surface morphology in Fig. 7. With the addition of POSS-NH₃⁺Cl-, the RB rejection presents an up-and-down trend as a function of the catechol/POSS mass ratio. Meanwhile, the permeance exhibited a “trade-off” trend. The optimal membrane performance with a permeance of 3.85 L m⁻² h⁻¹ bar⁻¹ and RB rejection of 87% was obtained at a POSS-NH₃⁺Cl-/catechol mass ratio of 5:1. The initial decrease in permeance is probably due to the fact that a continuous layer of POSS-NH₃⁺Cl-/catechol coating is gradually formed on the surface of the PI support and, which could enhance solvent permeation resistance. As a result, the EtOH permeance decreased from 184 L m⁻² h⁻¹ bar⁻¹ to 3.85 L m⁻² h⁻¹ bar⁻¹ and RB rejection increased from 10%–87%.

However, when further increasing POSS-NH₃⁺Cl-/catechol mass ratio to 10:1, the co-deposition amount lessened and membrane surface became less hydrophobic, leading to an increased permeance and decreased RB rejection. So, the mass ratio of POSS-NH₃⁺Cl-/catechol was fixed at 5:1 in the following tests.

Fig. 11(B) shows the membrane performance with aspect to different coating time. The permeance decreased and RB rejection increased as prolonging the coating time. Thickness of the functional layer may gradually increase with coating duration, which increasing permeation resistance. The EtOH permeance decreased from 30 L m⁻² h⁻¹ bar⁻¹ to 1.26 L m⁻² h⁻¹ bar⁻¹, while RB rejection increased from 9% to 99% when prolong coating time to 3 h. With further increase of coating time, the effective rejection of RB was achieved; however, the permeation resistance increased and permeance decreased continuously. Collectively, the POSS-NH₃⁺Cl-/catechol coating was optimized in terms of coating ratio and duration. A POSS-NH₃⁺Cl-/catechol ratio of 5:1 and a coating time of 3 h were employed in the following study.

3.4.2. Performance for separating various dyes

The separation of some low molecular weight dyes from EtOH is shown in Fig. 12. The optical images of feeds and filtrates of dye solutions were shown in Fig. A7. The chemical structures, molar weights and charges of these dyes were summarized in Fig. A8. The EtOH permeance for diﬀerent dyes has no signiﬁcant inﬂuence on solvent ﬂux. Dyes with relatively lower molecular weight exhibit better rejection.
higher molecular weight, such as RB (MW 1071) and MB (MW 800) were completely rejected, while other dyes were partly rejected. Despite its lower molecular weight, the CV rejection was slightly higher than OG rejection, and this could be related to the electrostatic repulsion between the amine groups on membrane surface and the positively charged CV, although the dielectric constant of EtOH is rather low (25.3 compared to 80.1 for water) [51].

### 3.4.3. Separation performance in various solvents and long term performance in DMF

Fig. 13(A) depicts that the separation performance of as-prepared membrane in various solvents. Thanks to the cross-linked structure of both PI support and hybrid selective layer, the composite membrane exhibited good separation performance in a variety of solvents, including harsh solvents such as THF, DCM and DMF, which are troublesome in OSN applications. No obvious trends between solvent permeance and dye rejection have been observed. In fact, the solvent transport mechanism through OSN membrane is more complex than aqueous applications. The membrane performances in organic solvent are related to the solvent properties (viscosity, molar volume and surface tension), mutual interactions between solvent and membrane, as well as between solvent and solute [52,53]. However, for the alcohol homologous series, the dependence of performance on solvent is clear. For example, the permeance of alcohol solvents are in the order of MeOH > EtOH > IPA. The highest permeance observed for MeOH could be due to its lowest molar volume and viscosity. On the other hand, the lowest permeance obtained for IPA could be attributed to its highest molar and viscosity [5]. In addition, RB rejections in the alcohol solvents showed an opposite trend with the permeance. These could be related to the convective coupling between solute and solvent, and the “dragging effect” of solvent [54].

Long term performance of compositied membrane was tested using solutions of RB in EtOH and DMF as feed. Fig. A9 shows that the membrane performances did not change over two days. A weight loss less than 0.4% was obtained in an immersion test of co-deposited membrane in DMF for two weeks, further demonstrating the stability of co-deposited membrane.

#### 3.4.4. Comparison of separation performance with some reported membranes

Table 2 summarizes the separation performance of reported TFN OSN membranes and a relevant composite membrane. The co-deposited membrane in this study shows a comparable MeOH permeance to the (PA/MOFs)/PI membranes containing MIL-53 or ZIF-8, although the solute rejection is a little lower [6]. Comparing with (PDMS/Zeolite)/PAN, which shows slightly higher rejections of a higher molecular weight solute, the co-deposited membrane in this study exhibits a 6.24 times higher toluene permeance and a 4.32 times higher DCM permeance [7].

It is intriguing to find that the membrane exhibits a 1.52 times higher MeOH permeance and 1.50 times greater IPA permeance than a recently reported catechol and polyethyleneimine co-deposited membrane with better or similar rejections [20]. Furthermore, we have conducted similar coating using dopamine or catechol/PEI to replace catechol/POSS-NH$_2$-Cl. As shown in Table 3, the (catechol/POSS)/PI still shows better separation performance than polydopamine/PI and (catechol/PEI)/PI. The cage pore diameter of a POSS is ca. 0.53 nm, which is in the range of typical nanofiltration [21]. One possible explanation is that comparing to the flexible organic matrix layer in catechol and polyethyleneimine co-deposited membrane, the rigid inorganic POSS cages could provide preferential flow path for small solvent molecule.

### 4. Conclusions

In summary, a one-step mussel-inspired co-deposition strategy has been discovered to fabricate novel nanocomposite OSN membranes. According to the chemical characterizations of membranes, the co-deposition mechanism is disclosed which is similar to that of dopamine
self-polymerization but without the involvement of intramolecular cyclization reaction. The mass ratio of POSS-NH$_2$-Cl/catechol is crucial to the physicochemical and separation properties of our developed membranes. The optimal nanocomposite membrane exhibited an ETOH permeance of 1.26 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ with RB rejection of 99%. Most importantly, the membrane can demonstrate good separation performance toward dyes in a wide range of organic solvents including challenging solvents such as THF, DCM and DMF contributed by the cross-linked structure of both PEI support and hybrid separating layer composing of unique inorganic POSS cages.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.memsci.2016.12.026.

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