Rapid co-deposition of graphene oxide incorporated metal-phenolic network/piperazine followed by crosslinking for high flux nanofiltration membranes

Yang, Yang; Li, Ye; Li, Qing; Wang, Yining; Tan, Choon Hong; Wang, Rong

2019

Yang, Y., Li, Y., Li, Q., Wang, Y., Tan, C. H. & Wang, R. (2019). Rapid co-deposition of graphene oxide incorporated metal-phenolic network/piperazine followed by crosslinking for high flux nanofiltration membranes. *Journal of Membrane Science*, 588, 117203-.
<https://dx.doi.org/10.1016/j.memsci.2019.117203>

<https://hdl.handle.net/10356/150780>

<https://doi.org/10.1016/j.memsci.2019.117203>

© 2019 Elsevier B.V. All rights reserved. This paper was published in *Journal of Membrane Science* and is made available with permission of Elsevier B.V.

Downloaded on 26 Apr 2023 19:07:34 SGT

Rapid co-deposition of graphene oxide incorporated metal-phenolic network/piperazine followed by crosslinking for high flux nanofiltration membranes

Yang Yang^{1,2}, Ye Li¹, Qing Li¹, Yining Wang¹, Choon Hong Tan³ and Rong Wang^{1, 4*}

1. *Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Singapore 637141*
2. *Interdisciplinary Graduate School, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798*
3. *Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371*
4. *School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798*

**Corresponding author: rwang@ntu.edu.sg*

Abstract

In this study, we presented a novel nanofiltration membrane fabrication strategy through rapid co-deposition of a versatile platform – metal phenolic networks (MPNs) and piperazine (PIP) on a porous substrate followed by trimesoyl chloride (TMC) crosslinking. Inspired by the catechol chemistry, tannic acid (TA) was functionalized to tether PIP monomers, and participated in the co-deposition via coordination bonds with Fe^{3+} ions on a substrate to form Fe^{3+} /TA-PIP complex. A series of analyses (SEM, XPS, FT-IR, water contact angle and zeta potential) confirmed the successful synthesis Fe^{3+} /TA-PIP deposition and polyamide (PA) layer. The resultant membrane exhibited water permeability of 13.73 LMH/bar and 89.52 % for MgSO_4 rejection. The fabrication was further improved by embedding modified graphene oxide (GO) nanosheets into the Fe^{3+} /TA-PIP complex. The optimized nanocomposite membrane achieved a water permeability at 21.66 LMH/bar, along with a well maintained MgSO_4 rejection at 91.25 % and $\text{NaCl}/\text{MgSO}_4$ selectivity (α) at 10.02 under 2 bar operation pressure. The rapid co-deposition mediated by nanomaterials incorporation provides an effective approach to design high performance thin film composite (TFC) membrane.

Keywords:

Nanofiltration; interfacial polymerization; co-deposition; metal-phenolic networks; graphene oxide.

Graphical abstract

1. Introduction

Nanofiltration (NF) membranes with pore size ranging from 0.5 to 2 nm have attracted great interests in various separation applications, such as water softening, dye purification, seawater pretreatment, etc., owing to their high water permeability, low operating pressure, and high selectivity of mono-/divalent salts [1-3]. Nowadays, commonly used commercial NF membranes are thin film composite (TFC) membranes, which are fabricated via interfacial polymerization (IP) technique [4]. Interfacial polymerization is a fast and reaction-diffusion heterogeneous system, in which two monomers (di-/tri-amine and acyl chlorides) crosslink to form a dense aromatic or semi-aromatic polyamide (PA) thin film at the interface [5,6]. Although this process is widely applied for the TFC membrane fabrication, the performance of developed TFC membrane still requires further improvement [7,8]. Current researches have focused on modifying IP procedures, such as optimization of reaction conditions [9], monomer substitution [10], utilization of hydrophilic additives [11,12] and porous substrate adjustment [13] to further enhance the separation properties. Another strategy to achieve high performance was the construction of nanocomposite membrane [14]. A variety of nanomaterials, including carbon nanomaterials, metal oxide, mesoporous materials and metal organic frameworks (MOFs) have been incorporated into the substrate polymer matrices or polyamide skin layer [15]. However, these improvement methods have limited elevation in separation performance, and the self-aggregation of nanomaterials easily caused defect formation on the surface, which was unsuitable for large scale membrane fabrication. As a consequence, a facile method is in demand for TFC membrane fabrication with high water permeability and salt rejection.

Based on catechol chemistry, a more rapid and environmental friendly method including plant-derived polyphenol and metal ions has attracted attention recently for conformal coating regardless of the substrate's pore size, shape or composition [16]. Three dimensional metal-

phenolic networks (MPNs), a versatile self-assembled supra-molecule, could be formed through reversible coordination bonds of polyphenol building blocks and metal ions within several minutes [17]. Tannic acid (TA) is one kind of star-shaped polyphenol with a hydrophobic core and hydrophilic chain commonly used in MPNs construction. Sufficient catechol and gallol groups were located on five arms in TA molecule, which provide chelating sites for metal ions (e.g., Fe^{3+} or Ni^{2+}) [18,19], and serve as a functional platform for secondary reactions, such as Michael or Schiff reaction [20-22]. Since the pioneer work from Caruso's group in year 2013 [23], several studies have applied MPNs coating method into membrane fabrication procedure as surface coating [24], interlayer for further IP step [25], or selective layer directly deposited on porous substrate [26,27]. Lin et al. reported that Fe^{3+} /TA nanofilm was directly deposited on a polyether sulfone (PES) substrate via layer-by-layer method and the resulting membrane achieved a water permeation of 12.4 LMH/bar and 99% rejection to methyl orange and sunset yellow [28]. However, the current research on MPNs in membrane science was still limited and pure MPNs deposited on membrane as a selective layer is not dense enough for inorganic salt rejection, which hinders their application in water desalination or ion separation process.

In this study, to the best of our knowledge, we reported a novel membrane fabrication approach via rapid co-deposition of MPNs with PIP incorporation followed with IP to construct TFC membrane for the first time. Possible chemical reactions and fabrication process were illustrated in Scheme 1. Considering porous PES substrate is negatively charged in a wide pH range, Fe^{3+} ions could be adsorbed via electrostatic interactions on the surface, which provided active sites for bonding with TA to form MPNs. Meanwhile, TA in aqueous phase was mixed with piperazine (PIP) to form TA-PIP complex through Michael addition reaction in basic condition. The resulting mixture was applied on the substrate membrane to form a controlled architecture of Fe^{3+} /TA-PIP complex. Subsequently, we performed IP of trimesoyl chloride

(TMC) crosslinking with PIP to form a selective layer on the top surface. The chemical and morphological structure of the resultant membranes were investigated during the fabrication procedure, and TA concentration was optimized for the best performance.

Moreover, we believed this result still has space for further improvement. Graphene oxide (GO), one type of two-dimensional (2D) nanosheets decorated with various oxygen-containing functional groups, was added into the TA-PIP aqueous solution. The modified GO nanosheets were confirmed to be successfully embedded into Fe^{3+} /TA-PIP complex, which led to the changes in surface morphology, hydrophilicity and zeta potential. The resultant nanocomposite NF membrane with optimized GO loading concentration achieves higher water flux under low operation pressure (2 bar) for divalent ion separation. It is expected that our study could provide a new approach to enhance membrane permeability while maintaining a high salt rejection and mono/divalent ion selectivity.

Scheme 1 (A) Possible process of gallol groups in Michael addition reaction, Fe³⁺/TA-PIP formation and connection with TMC, (B) Fabrication process of the TFC NF membrane mediated by co-deposition of Fe³⁺/TA-PIP

2. Experimental

2.1 Chemicals and materials

Polyethersulfone ultrafiltration (UF) sheet substrate (HPES, MWCO = 50 kDa) was supplied by MICRODYN-NADIR Pte. Ltd (Singapore). Tannic acid (TA, puriss), iron (III) chloride hexahydrate (FeCl₃·6H₂O, puriss, 98.0-102 %), phosphate buffered saline (PBS, tablet), graphene oxide (GO, 4 mg/mL, dispersion in H₂O, monolayer content >95 %), trimesoyl chloride (TMC, 98%), n-Hexane (anhydrous, 95 %), sodium chloride (NaCl, BioXtra, ≥99.5%) were all obtained from Sigma-Aldrich (Singapore). Piperazine (PIP, anhydrous for synthesis, ≥99 %), hydrochloric acid fuming (HCl, ACS, ISO, Reag. Ph Eur), sodium hydroxide (NaOH, ACS, Reag. Ph Eur, ISO), magnesium sulfate heptahydrate (MgSO₄·7H₂O, ACS, Reag. Ph Eur), sodium sulfate (Na₂SO₄, anhydrous for analysis), magnesium chloride hexahydrate

($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, ACS, ISO, Reag. Ph Eur), were purchased from Merck Pte. Ltd. (Singapore). Unless stated specifically, all chemical reagents were commercially obtained and used as received. Deionized water (DI) was collected from the Milli-Q ultra-pure water system (Millipore).

2.2 Preparation of PES- Fe^{3+} /TA-PA NF membrane

An aqueous solution for metal-phenolic networks (MNPs) deposition was prepared using a certain amount tannic acid (0.02, 0.05, 0.08, and 0.12 g) and 0.08 g piperazine dissolved in 40 ml PBS buffer solution ($\text{pH} = 7.4$) and stirred for 1 h under Ar protection to complete Michael addition reaction and form TA-PIP complex. PES UF substrate was first immersed into FeCl_3 solution for 10 min to ensure the iron ion adsorption on the surface of the support. A rubber roller was employed to remove excess aqueous solution on the PES support until the surface appears dull and dry. The TA-PIP solution was poured onto the Fe^{3+} impregnated substrate for 1.5 min to build up metal-phenolic networks with piperazine incorporation deposited on the membrane surface. The membrane surface was then rinsed with DI water to remove residual reactants and unstable MNPs. After membrane surface was dried by rubber roller, 0.1 % (wt./v) TMC n-hexane solution was poured onto PES- Fe^{3+} /TA-PIP for 1 min to initiate surface crosslinking. The result membrane was post-treated at 60 °C for 10 min for further polymerization. The PES- Fe^{3+} /TA-PA membrane was cooled to room temperature and stored in DI water for 24h before characterization and performance test. In this work, the Fe^{3+} /TA-PIP deposited UF membrane and cross-linked NF membrane is named as PES- Fe^{3+} /TAx-PIP and PES- Fe^{3+} /TAx-PA, where ‘x’ represents the tannic acid adding concentration (0.5, 1.25, 2, and 3 mg/ml), respectively.

2.3 Preparation of nanocomposite PES-Fe³⁺/TA-GO-PA NF membrane

For NF membrane fabrication, based on aforementioned method, the Fe³⁺ saturated substrate was first prepared and dried surface via rubber roller. For the aqueous solution preparation to be used for nanocomposite MPNs deposition, certain volume (1, 2 and 3 ml) of graphene oxide dispersion (4 mg/ml) was added into PBS buffer solution (0.01 M, pH 7.4) to reach 20 ml in three-necked flask. After ultrasonication for 15 min, tannic acid (0.02 g) dissolved in 10 mL buffer solution was slowly dropped into mixture and stirred at room temperature, followed by piperazine (0.08 g) dissolved in 10 ml PBS solution dropwise into the flask for 1 h in Ar atmosphere to complete Michael addition reaction and surface modification of GO nanosheets. The ending reaction mixture was ultrasonic for 10 min and directly poured onto the substrate for 1.5 min co-deposition. The membrane surface was then rinsed with DI water to remove residual reactants and unstable deposits. Until the surface appears dull and dry via roller treatment, a 0.1 % (wt./v) TMC/n-hexane solution was poured onto the PES-Fe³⁺/TA-GO-PIP for 1 min to conduct surface crosslinking procedure. The excess of organic solution was then drained off and the membrane was heated at 60 °C in an air-oven for 10 min. After cooled to room temperature, membrane PES-Fe³⁺/TA-GO-PA was stored in DI water for 24 h prior to characterization and performance test. According to the concentration of GO in aqueous phase (0.1, 0.2 and 0.3 mg/ml), the membrane was denoted as PES-Fe³⁺/TA_x-GO_y-PIP and PES-Fe³⁺/TA_x-GO_y-PA, where ‘y’ represent GO adding concentration.

To analyzing the surface property changes of GO during deposition solution preparation, 2 ml of graphene oxide dispersion (4 mg/ml) was added into PBS buffer solution (0.01 M, pH 7.4) to reach 20 ml in three-necked flask. After ultrasonication for 15 min, tannic acid (0.02 g) dissolved in 10 mL buffer solution was slowly dropped into mixture and stirred at room temperature for 0.5 h in Ar atmosphere. Piperazine (0.08 g) dissolved in 10 ml PBS solution was then added dropwise into the flask for another 0.5 h. The nanosheets were separated from

the buffer solution by centrifugation at the end of TA and PIP adding steps, washed with DI water to remove other residual reactants and finally freeze dried overnight. The resulting products named as TA-GO and TA-GO-PIP were collected for further characterization.

2.4 Materials and membrane characterizations

Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-1400 Plus (Japan) microscope operated at 120 kV. The TEM specimen was prepared via dropping solution on a copper grid supported with ultrathin carbon film and dried at room temperature. Field emission scanning electron microscope (FE-SEM) images were obtained on a JEOL FESEM 7600F (Japan) electron microscope operating at 5 kV coated with platinum. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu IR Prestige-21 (Japan) via the attenuated total reflection (ATR) holder to study chemical functional group changes. X-ray photoelectron spectroscopy (XPS) surveys were determined by using a Kratos AXIS Supra (UK) system with an Al K α X-ray monochromatic source. The binding energy scale was calibrated by setting the C1s peak at 284.8 eV. Zeta potentials of nanomaterials were detected by Zetasizer Nano ZEN3600 (Malvern, UK) in DTS1070 Zeta Potential cuvette. TA Instruments SDT Q600 (USA) was employed for thermogravimetric analysis (TGA) curve at a rate of 10 °C/min from 50 to 800 °C in N₂ atmosphere. Water contact angles (CA) were measured using a goniometer (Dataphysics OCA 15) by sessile drop method. Final values of contact angles were the average of at least five measurements. The zeta potentials of membrane surface were analyzed in the pH range from 3 to 9 using a zeta potential analyzer (SurPASS 3, Anton Paar, Austria). Data with correlation larger than 0.9995 was chosen as zeta potentials values. The surface topology and root-mean-squared roughness (Rq) were checked via an

atomic force microscope (AFM) Park Systems, NX10 (Korea) under the noncontact mode in the range of $5\ \mu\text{m} \times 5\ \mu\text{m}$.

2.5 Performance evaluation of NF membrane

The pure water flux and salt rejection of the thin film nanocomposite membrane were investigated by lab-scale dead-end filtration cell. The membrane was cut into diameter 4.2 cm round and pre-compacted at 3 bar for 30 minutes to ensure a steady performance. Membrane water flux and salt rejection were tested under 2 bar operation pressure. Permeate was collected in 5 min for 3 times with 10 min interval. The pure water flux was calculated by measuring the mass of the permeate. Water permeability, A , was calculated in following formula:

$$A = \frac{m_w}{\rho_w \cdot S \cdot \Delta P \cdot \Delta t} \quad (1)$$

where A is the water permeability (LMH/bar), m is the permeate weight in a certain time interval (g), ρ_w is the density of water at test temperature (g/L), S is the effective membrane area (m^2), ΔP and Δt are the trans membrane pressure (bar) and time interval (h), respectively.

Four different salts (MgSO_4 , MgCl_2 , Na_2SO_4 and NaCl) at 1000 ppm concentration as feed solution were tested to evaluate the separation performance of NF membrane, respectively. Salt rejection, R (%), and separation factor of NaCl to MgSO_4 (α) were calculated based on the following equations:

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100 \quad (2)$$

$$\alpha = \frac{1 - R_{\text{NaCl}}}{1 - R_{\text{MgSO}_4}} \quad (3)$$

C_p and C_f are the solute concentrations of the permeate and feed solution measured by conductivity meter (Ultrameter II, US), respectively. All these measurements were conducted at room temperature.

3. Results and discussion

3.1 Characterization and performance of Fe^{3+} /TA-PIP co-deposited membrane

Figure 1. Images of membrane surface changed during the fabrication procedure

The obvious color changes of the membrane surface during the Fe^{3+} /TA-PIP deposition and TMC crosslinking was shown in Figure 1. After Fe^{3+} /TA-PIP deposited on the membrane surface for 1.5 min, white PES substrate became violet in color. The surface morphology was examined via field emission scanning electron microscope (FESEM), as shown in Figure 2 and 3. The pristine PES substrate presented a smooth and loose surface morphology with the average pore size of 15 nm in Figure S1. After metal-phenolic networks Fe^{3+} /TA-PIP complex deposition on the surface (Figure 2A), there is no apparent difference compared to PES substrate except for the valley filled and the pore size of membrane was greatly reduced. Numerous papillae nanostructures were observed at a higher TA concentration because a rapid deposition might easily induce Fe^{3+} /TA-PIP aggregation. Some large pores (> 30 nm) could be clearly observed and parts of the pores were filled with Fe^{3+} /TA-PIP (Figure 2D). After building up polyamide layer by IP technique, as shown in Figure 3A, a nanobubble-like

structure could be identified on the membrane surface. This spherical globule morphology could be commonly observed in NF membranes, which is closely related to the properties of the substrate, diffusion rate of diamine and release of dissolved gas [29,30]. When the concentration of TA in aqueous phase increased, less globules and more defects was observed from Figures 3B, C and D

Figure 2. Front surface SEM images of PES-Fe³⁺/TAx-PIP prepared with different TA concentrations (x, mg/ml): (A) 0.5, (B) 1.25, (C) 2, and (D) 3, respectively. (PIP concentration set at 2 mg/ml)

Figure 3. SEM images of NF membrane PES-Fe³⁺/TAx-PA with different TA deposited concentrations (x, mg/ml): (A) 0.5, (B) 1.25, (C) 2, and (D) 3, respectively. (PIP concentration set at 2 mg/ml)

Chemical properties of Fe³⁺/TA-PIP and polyamide thin film coating on membrane surface were investigated via Fourier Transform Infrared (FT-IR) spectra and X-ray photoelectron spectroscopy (XPS) characterization; the results are shown in Figure 4, Figure S2 and the element contents of different samples are listed in Table 1. From Figure 4A, compared with pristine PES substrate, the membranes coated with Fe³⁺/TA-PIP and further polyamide layer had characteristic peaks at 1440 and 1540 cm⁻¹, which were attributed to phenolic group and quinone structure [31]. A broad peak at 3400 cm⁻¹ appeared in Figure S2 due to the –OH group of TA and –NH group of PIP. PES-Fe³⁺/TA0.5-PA had an intensified peak at 1620 cm⁻¹, which was corresponding to C=O bonds in amide structure [32]. The XPS characterization for thin films is showed in Figure 4B and the corresponding element contents from wide scan are listed in Table 1. It can be seen that, iron could be detected in the intermediate products PES-Fe³⁺/TA0.5-PIP, which confirmed that the Fe³⁺ ion was successfully adsorbed on the membrane surface and participated into Fe³⁺/TA-PIP network. Fe³⁺/TA-PIP complex on the surface

increased the percentage of oxygen from 15.52% to 22.99% and nitrogen from 2.26% to 5.5%; in the meantime, the percentage of sulfur was reduced from 6.39% to 1.33%. After TMC was used to crosslink PIP via IP, sulfur and iron could not be detected on the membrane surface. The atom percentage of carbon was apparently increased to 84.21% and oxygen content was reduced by more than 50%. The decreased O to N ratio from 4.18 to 2.20 further suggested successful formation of polyamide skin layer deposited onto the surface. C 1s high resolution spectra for controlled group PES-Fe³⁺/TA0.5-PA was deconvoluted and presented in **Figure S3**. The TFC membrane showed three peaks C-C/C-H, C-N/C-O, and C=O with binding energy at 284.8, 285.9 and 288.3 and the percentage of each peak was 68.59%, 25.35% and 6.06%, respectively [33].

Figure 4. (A) FT-IR (wavenumber 1800 – 800 cm⁻¹) and (B) XPS spectra of PES substrate, PES-Fe³⁺/TA0.5-PIP, and PES-Fe³⁺/TA0.5-PA

Table 1 Element content analysis from the XPS spectra of membranes

Sample	Atom percentage (%)					O:N Ratio
	C	N	O	S	Fe	
PES	75.83	2.26	15.52	6.39	/	6.87
PES-Fe ³⁺ /TA0.5-PIP	70.08	5.50	22.99	1.33	0.10	4.18
PES-Fe ³⁺ /TA0.5-PA	84.21	4.93	10.86	/	/	2.20

In order to compare the hydrophilicity of the membrane surface, water contact angle (WCA) was measured and the results are shown in Figure 5. The PES substrate had water contact angle of 32.1° after water dropped on the membrane surface for 5 seconds, which was attributed to large surface porosity with high water penetration. While the surface was coated with Fe³⁺/TA-PIP complex, (as shown in Figure 5), the water contact angle slight increased to 49.8° at 0.5 mg/ml TA adding, which could be responsible to the dense deposited layer with crosslinking of TA and PIP reduced pore size. When the ratio of TA to PIP concentration increased, the water contact angle largely decreased to 14.02° at TA concentration at 3 mg/ml. The more TA in aqueous phase, the more hydrophilic gallol and catechol groups occupied the surface. On the other hand, the IP procedure built up a dense polyamide skin layer, which turned PES-Fe³⁺/TA0.5-PA surface more hydrophobic with contact angle of 55.60°. The concentration of TA in aqueous could also affect the hydrophilicity of polyamide skin layer. The contact angle was reduced to 47.7° for 3 mg/ml TA added. The surface charge profiles of the pristine and coated membrane as a function of pH ranging from 3 to 9 are presented in Figure S4. The pristine PES substrate has the most negative potential and the value of membrane PES-Fe³⁺/TA0.5-PA was increased but still below zero in the entire pH range, which was attributed to the phenolic group in TA and the residential carboxyl group for acid chloride.

Figure 5. Water contact angle (WCA) of PES-Fe³⁺/TAx-PIP, and PES-Fe³⁺/TAx-PA membranes synthesized at different TA concentrations (x, mg/ml).

Figure 6 presents the separation performance of the MNPs/PIP co-deposited membrane PES-Fe³⁺/TA-PIP and PES-Fe³⁺/TA-PA NF membranes. As shown in **Figure 6**, without TMC crosslinking on membrane surface, co-deposited membrane PES-Fe³⁺/TA0.5-PIP exhibited high water permeability at 64.68 LMH/bar, but low salt rejection 10.48 % for MgSO₄. When PA layer was formed on the top surface, the pure water permeability experienced a downward trend from 13.73 LMH/bar to 9.47 LMH/bar with TA concentration increased from 0.5 to 3 mg/ml, which was caused by the combined effects of hydrophilicity and dense polyamide layer formation. Although a higher TA concentration could reduce the contact angle of PES-Fe³⁺/TA-PIP and PES-Fe³⁺/TA-PA, it could increase the thickness of deposited layer, resulting in a reduction in water permeation, as illustrated in **Figure S10**. A lower TA concentration in aqueous phase could be beneficial for increase membrane water permeability. A lower concentration of TA added presented better separation performance at 89.52 %. The change in salt rejection with varied TA concentration could be explained by defects formation. When TA concentration was too higher than PIP concentration, most of PIP might be connected with TA molecules. When TMC in n-hexane was poured on the membrane surface, the area without

diamine distribution could cause defects formation. This result was confirmed with SEM images observation as shown in **Figure 3**. Therefore, the optimized TA concentration for experiment was set at 0.5 mg/ml in aqueous phase for further optimization.

Figure 6. Membrane separation properties of PES-Fe³⁺/TA0.5-PIP without IP step, and PES-Fe³⁺/TAx-PA with different TA concentrations (x, mg/ml)

3.2 Characterization and investigation of GO surface property changes

The basic characterization of pristine GO nanosheets is presented in **Figure 7**. **Figure 7A and B** show the TEM and SEM images of the wrinkled and transparency structure owing to their atomic thickness, with a lateral size of a few micrometers. The functional groups were further confirmed by FTIR spectra, as shown in **Figure 7C**. The characteristic peaks of the pristine GO were observed at 3400 cm⁻¹ (-O-H stretch), 1734 cm⁻¹(carboxyl stretching vibration of -O-C=O), 1624 cm⁻¹(unoxidized C=C stretch), 1388cm⁻¹(-C-OH group bending vibration), 1220 cm⁻¹ (epoxy group C-O-C) and 1049 cm⁻¹(alkoxy groups C-O), which are confirmed by literatures [34]. The XPS measurement was carried out to evaluate the elemental composition and chemical bonding of nanosheets. From the XPS wide scan (**Figure 7D**), two distinct peaks C1s and O 1s were observed for pristine GO. The detail element contents are shown in Table S1. GO showed the ratio of C and O with 2.52 and deconvolution of pristine GO C1s peak

(Figure 7E) is composed of 38.42 % of C-C/C=C located at 284.8 eV, 49.65% of C-O bond at 286.8 eV and 11.93 % of C=O bond at 288.2 eV [35].

Figure 7. Characterizations of GO nanosheets. (a) TEM, (b) SEM, (c) FT-IR, (d) wide scan XPS, and (e) narrow scan and peak fitting of C 1s.

For the analysis of GO surface properties in TA-PIP solution, 2D nanosheets were collected via centrifugation and cleaned with DI water. The GO sheets dispersed in TA solution and TA-PIP solution were named as TA-GO and TA-GO-PIP, respectively, and the characterization results are presented in Figure 8. As shown in Figures 8A and B, the TEM images of TA-GO and TA-GO-PIP became black after the irradiation of electron beam and appeared to stick together with blunt edges, but 2D structure was still well-maintained and found at the edge of the sample. For FT-IR spectra in Figure 8C, compared with the spectra of pure GO (Figure 7C), several new characteristic peaks of TA-GO were observed at 1446 cm^{-1} , 1200 cm^{-1} , 871 cm^{-1} and 761 cm^{-1} , which were assigned to the TA phenolic group, TA ester groups and C-H bending vibration in gallol and catechol groups, respectively [36,37]. For TA-GO-PIP, a new peak at 1062 cm^{-1} was found of -C-N stretching vibration in piperazine connection, while peaks at 1734 cm^{-1} and 1624 cm^{-1} were merged into a single peak at 1614 cm^{-1} , which was attributed to

benzoquinone structure with high intensity absorption [38]. All these results proved that the GO nanomaterials were given surface modification in TA-PIP solution. TA with a large amount of aromatic structure could be easily adsorbed on the surface owing to the π - π interaction or attached via opening the epoxy ring on GO [39,40]. Diamine piperazine could participate in opening the epoxy ring on GO nanosheets in alkaline solution, or tethering on the TA gallol group via Michael addition. The proposed surface modification process is shown in Scheme 2.

Figure 8. Connection of TA and PIP molecules on the GO nanosheets. TEM images of (A)TA-GO, (B) TA-GO-PIP. (C) FT-IR and (D) XPS wide scan spectra of surface modified TA-GO and TA-GO-PIP. Narrow scan and peak fitting of C 1s (E) TA-GO and (F) TA-GO-PIP

Scheme 2. Surface modification process of GO with TA and PIP attachment

The modified GO nanosheets into TA-GO-PIP was further confirmed via XPS analysis. After TA was grafted on the surface of GO, the percentage of O contents was increased and C to O

ratio was reduced. The N 1s peak was detected in the sample TA-GO-PIP, with 7.32% of total elements. The C to O ratio for TA-GO-PIP was increased to 3.34, because of no oxygen in PIP molecule. The deconvolutions of sample TA-GO and TA-GO-PIP C1s peak are exhibited in **Figures 8E** and **F** and the composition of different bonds are listed in Table S1. TA coating on the surface increased the percentage of C-O bond and highly reduced the C=O bond contents. For sample TA-GO-PIP, two separated peaks (C-C/C=C and C-O) were merged into one broad peak because of C-N peak (285.8 eV) appearance [41,42]. The percentage of C-O bond was reduced and the C=O bond was slightly increased compared with pristine GO, which confirmed that parts of PIP molecule were participated in Michael reaction to TA. The modification of pristine GO by TA and PIP was also confirmed by thermal stability analysis via TGA curve and surface charge properties via zeta potential, as illustrated in **Figures S5 and S6**.

3.3 Characterization and performance of Fe³⁺/TA-GO-PIP co-deposited membrane

With GO participated in the formula, the surface morphologies of nanocomposite Fe³⁺/TA-GO-PIP and Fe³⁺/TA-GO-IP membranes were checked via FESEM, as shown in **Figure 9**. TA concentration was set at 0.5 mg/ml based on aforementioned result. For TA-GO-PIP incorporation in the deposit (**Figure 9A**), nanosheets could be observed and the remaining surface area was consistent with sample PES-Fe³⁺/TA0.5-PIP. After polyamide layer was formed on the top surface, a large quantity of volcano structure was observed with a ring diameter around 50 nm. The structure is assumed to be formed through PIP eruption from membrane surface pores and further crosslinking with initial polyamide tufts in the interface [43]. Increasing nanosheets addition could enlarge the ring diameter as shown in **Figures 9C and D**. With more nanosheets residential on the membrane coating layer, the surface pore size could be smaller and PIP diffusion rate to the organic phase could be largely reduced. Thus

less polyamide tuft seeds were taken shape at the beginning of cross-linking and the aqueous phase monomers on the substrate surface might need a long diffusion route to form a complete thin film [44].

Figure 9. Front surface SEM images of (A) PES-Fe³⁺/TA-GO0.1-PIP and PES-Fe³⁺/TA-GOy-PA prepared with different GO concentrations (y, mg/ml): (B) 0.1, (C) 0.2, (D) 0.3. (TA concentration set at 0.5 mg/ml)

It can be seen from the FT-IR spectra, compared with **Figure 4A**, GO loading widened the peak at 1640 cm⁻¹ for sample PES-Fe³⁺/TA-GO-PIP, which was attributed to the various C=O bonds in GO. The characteristic peak of GO shown in **Figure 10A** was overlapped by PES substrate and Fe³⁺/TA-PIP coating due to less percentage of GO in the coating layer. For XPS analysis, the membrane with GO loading had a higher carbon atomic percentage and lower O to N ratio compared with the controlled group, which could be explained by a higher proportion of carbon in GO nanosheets and an increase in crosslinking degree of TMC with PIP. In order to further investigate the GO loading effect on the top surface, C 1s high resolution spectra for PES-Fe³⁺/TA-GO0.2-PA was deconvoluted and presented in **Figure S8**. From the functional group

percentage table (Table S2), a higher percentage for C-C/C-H bond was found, which is attributed to GO with a large proportion of carbon bond. The composition of polyamide layer without/with modified GO loading was nearly same, which suggested the GO embedded into Fe^{3+} /TA-PIP complex did not affect the skin layer formation.

Figure 10. (A) FT-IR (wavenumber 1800 – 800 cm^{-1}) and (B) XPS spectra of PES- Fe^{3+} /TA-GO0.2-PIP and PES- Fe^{3+} /TA-GO0.2-PA (TA concentration was set at 0.5 mg/ml)

Table 2 Element content analysis from the XPS spectra of nanocomposite membranes

Sample	Atom percentage (%)					O:N Ratio
	C	N	O	S	Fe	
PES- Fe^{3+} /TA-GO0.2-PIP	75.05	4.10	17.05	3.62	0.18	4.16
PES- Fe^{3+} /TA-GO0.2-PA	86.92	4.29	8.76		0.03	2.04

The hydrophilicity of the membrane surface and the surface charge profiles were also checked and shown in Table S3 and Figure S4. A lot of oxygen containing hydrophilic groups on the

TA-GO-PIP reduced the water contact angle of PES-Fe³⁺/TA-GO0.1-PIP sample. However, the functionalized GO nanosheets remarkably elevated the water contact angle after IP step. The water contact angle changed from 59.1 to 69.4° for 0.1 to 0.3 mg/ml modified GO mixed, which was attributed to surface roughness increase as shown [Figure 9](#). For surface zeta potential, TA-GO-PIP loaded on the membrane surface could reduce the zeta potential compared with PES-Fe³⁺/TA0.5-PA. It shows that increasing nanosheets complex concentration, the membrane surface changed to more negatively charged, which was due to the abundant oxygen containing group dissociation in GO complex. All these changes confirm the successful TA-GO-PIP incorporation into Fe³⁺/TA-PIP complex and the nanosheets loading did not obstruct the interfacial polymerization on the top surface.

The impact of GO loading in the deposited layer of the TFC membranes were investigated and separation performances are shown in [Figure 11](#). The water permeability of PES-Fe³⁺/TA-GO-PA membrane increased from 21.66 LMH/bar to 23.21 LMH/bar with increasing GO mixing from 0.1 to 0.3 mg/ml. In all, the water permeability for TA-GO-PIP embedded membrane was much higher than group of PES-Fe³⁺/TA0.5-PA at 13.73 LMH/bar. The enhanced water flux could be explained by the changes of surface roughness [as illustrated in Figure S9](#), hydrophilicity and thickness of Fe³⁺/TA-PIP complex caused by GO incorporation [\[45\]](#). With GO concentration increased, the membrane was changed to more hydrophilic, and TA-GO-PIP mixed in aqueous would be beneficial for thin Fe³⁺/TA-PIP complex formation. The salt rejection of TA-GO-PIP loaded membrane exhibited slight higher than control group and followed the order of Na₂SO₄ ~ MgSO₄ > MgCl₂ > NaCl, which is a typical negatively charged NF desalination performance. The highest MgSO₄ rejection (91.25 %) was achieved with TA-GO-PIP loaded at 0.1 mg/ml, with NaCl/MgSO₄ to be selective ($\alpha=10.02$). When GO loading concentration was increased to 3 mg/ml, the MgSO₄ rejection was slightly decreased to 87.06 % and Na₂SO₄ rejection was increased to 87.60 %. Generally, the unbalanced dispersion of TA-

GO-PIP in the deposited layer at a higher concentration could potentially affect the polyamide layer formation, which led to a lower rejection of salt at a higher TA-GO-PIP concentration. Moreover, TA-GO-PIP incorporation could enhance negative charges on PA surface (Figure S4) and strengthen the Donnan exclusion, which explained the higher rejection of MgSO_4 compared with MgCl_2 and the increase of Na_2SO_4 rejection at a higher TA-GO-PIP concentration [46,47].

Figure 11. Membrane separation properties of $\text{PES-Fe}^{3+}/\text{TA-GO}_y\text{-PA}$ with various GO loading concentrations (y, mg/ml)

The performance comparison of the membrane in this work with commercial and literature reported NF membranes is summarized in Table 3. It can be seen that the newly developed membrane $\text{PES-Fe}^{3+}/\text{TA-GO0.1-PA}$ exhibited good pure water permeability while maintaining high salt selectivity under a low operation pressure of 2 bar. This result was attributed to the effective PA selective layer with low defects rate and narrow size distribution formed under controlled diffusion of PIP monomer [48]. The TA-GO-PIP incorporated into the deposited layer further eliminated the large surface pores of the substrate, which could avoid polyamide cross-linked to form protuberances inside the porous structure and reduced the membrane resistance [25]. In addition, the presence of GO nanosheets in $\text{Fe}^{3+}/\text{TA-PIP}$ deposited layer could impede the $\text{Fe}^{3+}/\text{TA-PIP}$ growing up and generate interfacial voids between

nanocomposite and polymer matrices for a looser structure [49]. The GO laminates decorated by TA could provide molecular sieving ability because of interlayer space and abundant oxygen-containing groups [50]. Thus PES-Fe³⁺/TA-GO0.1-PA membrane presented enhanced water flux and monovalent-divalent salt selectivity.

Table 3. Comparison of various NF membranes

Membrane	Water permeability (LMH/bar)	Solute rejection (%)				Operating pressure (bar)	Ref.
		MgSO ₄	MgCl ₂	Na ₂ SO ₄	NaCl		
PEI/PIP TFC NF	18.2	93.8	96.3	77.4	53.6	2	[47]
TFC _n NF	19.6	96.0	57.5	97.8	17.5	3.4	[25]
PIP-GO TFN	18.1	91.2	73.1	/	31.6	4.1	[51]
TA-GOQD TFN	11.7	31.2	11.5	66.7	17.2	2	[52]
PA attached PDA modified PAN	25.1	98.0	45.5	99.0	27.5	4	[53]
DOW NF-270	11.3	94.7	/	98.6	/	4	[54]
PES-Fe ³⁺ /TA0.5-PA	13.7	89.5	/	/	/	2	This work
PES-Fe ³⁺ /TA-GO0.1-PA	21.7	91.2	32.7	84.0	10.8	2	This work

4. Conclusions

In this study, we reported a novel approach for fabricating NF membrane with high water permeability while maintaining high salt rejection for divalent ions. MPNs as a versatile platform was rapidly co-deposited with PIP to form a coating layer on PES membrane substrate within 1.5 min, followed by IP to form a skin layer within 1 min contact time. A series of analyses (SEM, XPS, FT-IR, water contact angle and zeta potential) confirmed the successful synthesis PA on the surface and the membrane PES-Fe³⁺/TA0.5-PA exhibited water permeability of 13.73 LMH/bar with 89.52 % MgSO₄ rejection. After the optimization of TA concentration, GO nanosheets was employed to construct nanocomposite Fe³⁺/TA-GO-PIP matrices for further enhancement of membrane separation performance. The TA-GO-PIP was

confirmed to be incorporated into the deposited layer, which affected PIP diffusion rate, resulting in a volcano-like structure appeared in the PA skin layer. The membrane PES-Fe³⁺/TA-GO0.1-PA achieved the water permeability of 21.66 LMH/bar, MgSO₄ rejection at 91.25 % and NaCl/MgSO₄ selectivity at 10.02 under 2 bar operation pressure. This work provides a novel fabrication strategy to rapidly co-deposit a versatile platform for controlled interfacial polymerization, which has great potential applied in large scale NF membrane fabrication.

Acknowledgements

We appreciate Xiaofei You for helpful discussions. We would like to thank Ms. Janelle Ng Ru Ying and Ms. Lam Mei Shan for characterization support. This work was supported by PUB, Singapore's National Water Agency and a grant from the Singapore National Research Foundation (EWI 1501-IRIS-04). The funding support from Singapore Economic Development Board to the Singapore Membrane Technology Centre (SMTTC) is gratefully acknowledged.

References

- [1] R.J. Petersen, Composite Reverse-Osmosis and Nanofiltration Membranes, *J. Membr. Sci.*, 83 (1993) 81-150.
- [2] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, *Science*, 333 (2011) 712-717.
- [3] A.W. Mohammad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal, Nanofiltration membranes review: Recent advances and future prospects, *Desalination*, 356 (2015) 226-254.
- [4] J.R. Werber, C.O. Osuji, M. Elimelech, Materials for next-generation desalination and water purification membranes, *Nat. Rev. Mater.*, 1 (2016) 16018.
- [5] B.S. Lalia, V. Kochkodan, R. Hashaikheh, N. Hilal, A review on membrane fabrication: Structure, properties and performance relationship, *Desalination*, 326 (2013) 77-95.
- [6] Z. Tan, S. Chen, X. Peng, L. Zhang, C. Gao, Polyamide membranes with nanoscale Turing structures for water purification, *Science*, 360 (2018) 518-521.
- [7] H.B. Park, J. Kamcev, L.M. Robeson, M. Elimelech, B.D. Freeman, Maximizing the right stuff: The trade-off between membrane permeability and selectivity, *Science*, 356 (2017) eaab0530.
- [8] A.G. Fane, R. Wang, M.X. Hu, Synthetic membranes for water purification: status and future, *Angew. Chem. Int. Ed. Engl.*, 54 (2015) 3368-3386.
- [9] C.L. Kong, M. Kanezashi, T. Yamamoto, T. Shintani, T. Tsuru, Controlled synthesis of high performance polyamide membrane with thin dense layer for water desalination, *J. Membr. Sci.*, 362 (2010) 76-80.
- [10] L.F. Liu, Z.B. Cai, J.N. Shen, L.X. Wu, E.M.V. Hoek, C.J. Gao, Fabrication and characterization of a novel poly (amide-urethane@imide) TFC reverse osmosis membrane with chlorine-tolerant property, *J. Membr. Sci.*, 469 (2014) 397-409.
- [11] L. Zhao, P.C.Y. Chang, W.S.W. Ho, High-flux reverse osmosis membranes incorporated with hydrophilic additives for brackish water desalination, *Desalination*, 308 (2013) 225-232.
- [12] B. Khorshidi, T. Thundat, D. Pernitsky, M. Sadrzadeh, A parametric study on the synergistic impacts of chemical additives on permeation properties of thin film composite polyamide membrane, *J. Membr. Sci.*, 535 (2017) 248-257.
- [13] W.A. Suwaileh, D.J. Johnson, S. Sarp, N. Hilal, Advances in forward osmosis membranes: Altering the sub-layer structure via recent fabrication and chemical modification approaches, *Desalination*, 436 (2018) 176-201.
- [14] W.J. Lau, S. Gray, T. Matsuura, D. Emadzadeh, J.P. Chen, A.F. Ismail, A review on polyamide thin film nanocomposite (TFN) membranes: History, applications, challenges and approaches, *Water Res.*, 80 (2015) 306-324.
- [15] T. Humplik, J. Lee, S.C. O'Hern, B.A. Fellman, M.A. Baig, S.F. Hassan, M.A. Atieh, F. Rahman, T. Laoui, R. Karnik, E.N. Wang, Nanostructured materials for water desalination, *Nanotechnology*, 22 (2011) 292001.
- [16] J. Guo, Y. Ping, H. Ejima, K. Alt, M. Meissner, J.J. Richardson, Y. Yan, K. Peter, D. von Elverfeldt, C.E. Hagemeyer, F. Caruso, Engineering Multifunctional Capsules through the Assembly of Metal-Phenolic Networks, *Angew. Chem.*, 126 (2014) 5652-5657.
- [17] H. Ejima, J.J. Richardson, F. Caruso, Metal-phenolic networks as a versatile platform to engineer nanomaterials and biointerfaces, *Nano Today*, 12 (2017) 136-148.

- [18] H. Wu, H. Sun, W. Hong, L. Mao, Y. Liu, Improvement of Polyamide Thin Film Nanocomposite Membrane Assisted by Tannic Acid-Fe(III) Functionalized Multiwall Carbon Nanotubes, *ACS Appl. Mater. Interfaces*, 9 (2017) 32255-32263.
- [19] F. You, Y. Xu, X. Yang, Y. Zhang, L. Shao, Bio-inspired Ni(2+)-polyphenol hydrophilic network to achieve unconventional high-flux nanofiltration membranes for environmental remediation, *Chem. Commun. (Camb.)*, 53 (2017) 6128-6131.
- [20] W.Z. Qiu, H.C. Yang, L.S. Wan, Z.K. Xu, Co-deposition of catechol/polyethyleneimine on porous membranes for efficient decolorization of dye water, *J. Mater. Chem. A*, 3 (2015) 14438-14444.
- [21] Q. Lyu, J. Zhang, K.G. Neoh, C. Li Lin Chai, A one step method for the functional and property modification of DOPA based nanocoatings, *Nanoscale*, 9 (2017) 12409-12415.
- [22] G.H. Liu, Z.Y. Jiang, C. Chen, L.P. Hou, B.X. Gao, H. Yang, H. Wu, F.S. Pan, P. Zhang, X.Z. Cao, Preparation of ultrathin, robust membranes through reactive layer-by-layer (LbL) assembly for pervaporation dehydration, *J. Membr. Sci.*, 537 (2017) 229-238.
- [23] H. Ejima, J.J. Richardson, K. Liang, J.P. Best, M.P. van Koeveerden, G.K. Such, J. Cui, F. Caruso, One-step assembly of coordination complexes for versatile film and particle engineering, *Science*, 341 (2013) 154-157.
- [24] H. Guo, Z.K. Yao, Z. Yang, X.H. Ma, J.Q. Wang, C.Y.Y. Tang, A One-Step Rapid Assembly of Thin Film Coating Using Green Coordination Complexes for Enhanced Removal of Trace Organic Contaminants by Membranes, *Environ. Sci. Technol.*, 51 (2017) 12638-12643.
- [25] Z. Yang, Z.W. Zhou, H. Guo, Z. Yao, X.H. Ma, X. Song, S.P. Feng, C.Y. Tang, Tannic Acid/Fe(3+) Nanoscaffold for Interfacial Polymerization: Toward Enhanced Nanofiltration Performance, *Environ. Sci. Technol.*, 52 (2018) 9341-9349.
- [26] H.J. Kim, D.G. Kim, H. Yoon, Y.S. Choi, J. Yoon, J.C. Lee, Polyphenol/FeIII Complex Coated Membranes Having Multifunctional Properties Prepared by a One-Step Fast Assembly, *Adv. Mater. Interfaces*, 2 (2015) 1500298.
- [27] T. Chakrabarty, L. Perez-Manriquez, P. Neelakanda, K.V. Peinemann, Bioinspired tannic acid-copper complexes as selective coating for nanofiltration membranes, *Sep. Purif. Technol.*, 184 (2017) 188-194.
- [28] C.E. Lin, M.Y. Zhou, W.S. Hung, B.K. Zhu, K.R. Lee, L.P. Zhu, L.F. Fang, Ultrathin nanofilm with tailored pore size fabricated by metal-phenolic network for precise and rapid molecular separation, *Sep. Purif. Technol.*, 207 (2018) 435-442.
- [29] X.H. Ma, Z.K. Yao, Z. Yang, H. Guo, Z.L. Xu, C.Y.Y. Tang, M. Elimelech, Nanofoaming of Polyamide Desalination Membranes To Tune Permeability and Selectivity, *Environ. Sci. Technol. Lett.*, 5 (2018) 123-130.
- [30] Z.W. Jiang, S. Karan, A.G. Livingston, Water Transport through Ultrathin Polyamide Nanofilms Used for Reverse Osmosis, *Adv. Mater.*, 30 (2018) 1705973.
- [31] S.C. Han, W.D. He, J. Li, L.Y. Li, X.L. Sun, B.Y. Zhang, T.T. Pan, Reducible Polyethylenimine Hydrogels with Disulfide Crosslinkers Prepared by Michael Addition Chemistry as Drug Delivery Carriers: Synthesis, Properties, and In Vitro Release, *J Polym Sci Pol Chem*, 47 (2009) 4074-4082.
- [32] W.X. Fang, L. Shi, R. Wang, Interfacially polymerized composite nanofiltration hollow fiber membranes for low-pressure water softening, *J. Membr. Sci.*, 430 (2013) 129-139.
- [33] R.R. Xing, W. Wang, T.F. Jiao, K. Ma, Q.R. Zhang, W. Hong, H. Qiu, J.X. Zhou, L.X. Zhang, Q.M. Peng, Bioinspired Polydopamine Sheathed Nanofibers Containing Carboxylate Graphene Oxide Nanosheet for High-Efficient Dyes Scavenger, *ACS Sustain. Chem. Eng.*, 5 (2017) 4948-4956.
- [34] M. Hu, B.X. Mi, Enabling Graphene Oxide Nanosheets as Water Separation Membranes, *Environ. Sci. Technol.*, 47 (2013) 3715-3723.

- [35] M.Y. Lim, H. Shin, D.M. Shin, S.S. Lee, J.C. Lee, Poly(vinyl alcohol) nanocomposites containing reduced graphene oxide coated with tannic acid for humidity sensor, *Polymer*, 84 (2016) 89-98.
- [36] J. Luo, J.P. Lai, N. Zhang, Y.B. Liu, R. Liu, X.Y. Liu, Tannic Acid Induced Self-Assembly of Three-Dimensional Graphene with Good Adsorption and Antibacterial Properties, *ACS Sustain. Chem. Eng.*, 4 (2016) 1404-1413.
- [37] H.M. Hegab, A. ElMekawy, T.G. Barclay, A. Micheltmore, L. Zou, C.P. Saint, M. Ginic-Markovic, Single-Step Assembly of Multifunctional Poly(tannic acid)-Graphene Oxide Coating To Reduce Biofouling of Forward Osmosis Membranes, *ACS Appl. Mater. Interfaces*, 8 (2016) 17519-17528.
- [38] J.R. Burie, A. Boussac, C. Boullais, G. Berger, T. Mattioli, C. Mioskowski, E. Nabadryk, J. Breton, Ftir Spectroscopy of Uv-Generated Quinone Radicals - Evidence for an Intramolecular Hydrogen-Atom Transfer in Ubiquinone, Naphthoquinone, and Plastoquinone, *J. Phys. Chem.*, 99 (1995) 4059-4070.
- [39] S. Zhao, S.C. Xie, Z. Zhao, J.L. Zhang, L. Li, Z.X. Xin, Green and High-Efficiency Production of Graphene by Tannic Acid Assisted Exfoliation of Graphite in Water, *ACS Sustain. Chem. Eng.*, 6 (2018) 7652-7661.
- [40] J. Li, G.Y. Xiao, C.B. Chen, R. Li, D.Y. Yan, Superior dispersions of reduced graphene oxide synthesized by using gallic acid as a reductant and stabilizer, *J. Mater. Chem. A*, 1 (2013) 1481-1487.
- [41] S. Park, J.H. An, R.D. Piner, I. Jung, D.X. Yang, A. Velamakanni, S.T. Nguyen, R.S. Ruoff, Aqueous Suspension and Characterization of Chemically Modified Graphene Sheets, *Chem. Mater.*, 20 (2008) 6592-6594.
- [42] X.B. Wang, Y.L. Qin, L.H. Zhu, H.Q. Tang, Nitrogen-Doped Reduced Graphene Oxide as a Bifunctional Material for Removing Bisphenols: Synergistic Effect between Adsorption and Catalysis, *Environ. Sci. Technol.*, 49 (2015) 6855-6864.
- [43] J. Zhu, L. Qin, A. Uliana, J. Hou, J. Wang, Y. Zhang, X. Li, S. Yuan, J. Li, M. Tian, J. Lin, B. Van der Bruggen, Elevated Performance of Thin Film Nanocomposite Membranes Enabled by Modified Hydrophilic MOFs for Nanofiltration, *ACS Appl. Mater. Interfaces*, 9 (2017) 1975-1986.
- [44] A.K. Ghosh, E.M.V. Hoek, Impacts of support membrane structure and chemistry on polyamide-polysulfone interfacial composite membranes, *J. Membr. Sci.*, 336 (2009) 140-148.
- [45] Y. Zhang, H. Sun, H. Sadam, Y. Liu, L. Shao, Supramolecular chemistry assisted construction of ultra-stable solvent-resistant membranes for angstrom-sized molecular separation, *Chem. Eng. J.*, 371 (2019) 535-543.
- [46] D. Vezzani, S. Bandini, Donnan equilibrium and dielectric exclusion for characterization of nanofiltration membranes, *Desalination*, 149 (2002) 477-483.
- [47] W.X. Fang, L. Shi, R. Wang, Mixed polyamide-based composite nanofiltration hollow fiber membranes with improved low-pressure water softening capability, *J. Membr. Sci.*, 468 (2014) 52-61.
- [48] X. Zhang, Y. Lv, H.C. Yang, Y. Du, Z.K. Xu, Polyphenol Coating as an Interlayer for Thin-Film Composite Membranes with Enhanced Nanofiltration Performance, *ACS Appl. Mater. Interfaces*, 8 (2016) 32512-32519.
- [49] J. Zhu, J. Wang, A.A. Uliana, M. Tian, Y. Zhang, Y. Zhang, A. Volodin, K. Simoons, S. Yuan, J. Li, J. Lin, K. Bernaerts, B. Van der Bruggen, Mussel-Inspired Architecture of High-Flux Loose Nanofiltration Membrane Functionalized with Antibacterial Reduced Graphene Oxide-Copper Nanocomposites, *ACS Appl. Mater. Interfaces*, 9 (2017) 28990-29001.

- [50] K.H. Thebo, X. Qian, Q. Zhang, L. Chen, H.M. Cheng, W. Ren, Highly stable graphene-oxide-based membranes with superior permeability, *Nat Commun*, 9 (2018) 1486.
- [51] R.R. Hu, Y.J. He, C.M. Zhang, R.J. Zhang, J. Li, H.W. Zhu, Graphene oxide-embedded polyamide nanofiltration membranes for selective ion separation, *J. Mater. Chem. A*, 5 (2017) 25632-25640.
- [52] C.F. Zhang, K.F. Wei, W.H. Zhang, Y.X. Bai, Y.P. Sun, J. Gu, Graphene Oxide Quantum Dots Incorporated into a Thin Film Nanocomposite Membrane with High Flux and Antifouling Properties for Low-Pressure Nanofiltration, *ACS Appl. Mater. Interfaces*, 9 (2017) 11082-11094.
- [53] J.Y. Zhu, J.W. Hou, R.J. Zhang, S.S. Yuan, J. Li, M.M. Tian, P.H. Wang, Y.T. Zhang, A. Volodin, B. Van der Bruggen, Rapid water transport through controllable, ultrathin polyamide nanofilms for high-performance nanofiltration, *J. Mater. Chem. A*, 6 (2018) 15701-15709.
- [54] W. Zhao, H.Y. Liu, N. Meng, M.P. Jian, H.T. Wang, X.W. Zhang, Graphene oxide incorporated thin film nanocomposite membrane at low concentration monomers, *J. Membr. Sci.*, 565 (2018) 380-389.