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Reverse osmosis nanocomposite membranes containing graphene oxides coated by tannic acid with chlorine-tolerant and antimicrobial properties

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ABSTRACT

Graphene oxides coated by tannic acid (GOT) can be obtained easily by the self-polymerization of tannic acid in basic buffer solution on a graphene oxide surface. Polyamide reverse osmosis nanocomposite membranes containing GOT in the active layer were prepared by the interfacial polymerization using an organic solution containing trimesoyl chloride and an aqueous solution containing *m*-phenylene diamine and GOT. The polyamide membrane containing GOT (PA-GOT) showed significantly improved performances such as water flux, chlorine resistance, and antimicrobial properties, compared to the polyamide membrane without any additives and the polyamide membranes containing only tannic acid and/or graphene oxide. These high performances of PA-GOT membrane could be ascribed to a various of advantageous properties of GOT such as improved hydrophilicity, oxidative stress capability, barrier property, and compatibility with the polymer matrix.

1. Introduction

Water purification technologies have received increased attention due to the urgent increase in fresh water demand [1,2]. Membrane-based desalination technologies such as nanofiltration (NF) and reverse osmosis (RO) process have been rapidly developed and widely used due to their many advantages. Low cost, low operating temperature and high production efficiency are a few of the advantages [1–3]. Although cellulose acetate (CA) membranes are firstly developed and used for the commercial RO process, the use of CA membranes in the RO process has been limited due to the degradation by microbiological attack, narrow available pH use range, and severe compaction at high pressure [4–6]. On the other hand, polyamide (PA) thin film composite (TFC) membranes have exhibited better separation performances, wider pH range, and better physical properties than CA membranes [6]. Therefore, PA-TFC membranes are the most widely used in the RO process [5,6]. In spite of the advantageous properties of PA-TFC membranes, the desalination processes using PA-TFC membranes still suffers from poor chlorine resistance and biofouling problems [5,7–15]. There have been many studies to surmount these disadvantages of PA-TFC membranes [5,8,11,13,16,17]. For example, PA-TFC membranes having silver nanoparticles on the membrane surface showed a significant reduction in number of live bacteria and suppressed biofilm formation [8]. PA-TFC membranes containing carbon nanomaterials also showed improved chlorine resistant properties [11,13–15]. However, to the best of our knowledge, no RO membranes having both antimicrobial and chlorine-tolerant properties have been reported yet.

Graphene and graphene oxide (GO) have been widely used as filler materials for polymer nanocomposites to impart thermal stability, oxidation stability, biocidal properties, and mechanical strength [11,17–20]. Furthermore, it was recently demonstrated that polymer nanocomposite membranes having graphene and its derivatives can have very high water permeability, high durability, and chlorine resistant properties due to the unique properties of carbon nano structures [11,14,21–26]. Especially, such high membrane performance was observed from the polymer membranes prepared using the well-modified graphene derivatives having useful functional groups that can improve miscibility with the polymer matrix and also can impart various functions [18,26]. Plant-induced natural polyphenols including tannic acid that can be easily obtained from common plants such as oak, green tea, and

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Table 1
Water flux and salt rejection values of the membranes.

Membrane type[a]	MPD [wt%][b]	TA [wt%, $\times 10^3$][b]	GO [wt%, $\times 10^3$][b]	GOT [wt%, $\times 10^3$][b]	Water flux [LMH]	Salt rejection [%]
LFC-1 (commercial)	–	–	–	–	36.58 ± 1.17	96.98 ± 0.69
PA	1	–[c]	–[c]	–[c]	32.11 ± 2.85	95.75 ± 1.24
PA	2	–[c]	–[c]	–[c]	34.21 ± 1.74	96.80 ± 0.85
PA	3	–[c]	–[c]	–[c]	32.67 ± 2.42	96.22 ± 1.68
PA-T	2	1	–[c]	–[c]	40.00 ± 2.91	88.82 ± 4.46
PA-T	3	1	–[c]	–[c]	39.41 ± 2.49	89.18 ± 5.06
PA-GO	2	–[c]	1	–[c]	36.41 ± 1.79	95.44 ± 1.07
PA-GO	3	–[c]	1	–[c]	38.66 ± 0.69	96.96 ± 0.60
PA-GOT	2	–[c]	–[c]	1	37.33 ± 0.99	95.97 ± 0.65
PA-GOT	3	–[c]	–[c]	1	38.18 ± 1.16	96.32 ± 0.67
PA-T-GO	2	0.5	0.5	–[c]	38.89 ± 3.25	90.58 ± 4.58
PA-T-GO	3	0.5	0.5	–[c]	37.15 ± 4.54	90.92 ± 3.46

[a] The concentration of TMC organic solution for interfacial polymerization is 0.1 wt%.
[b] The concentration in aqueous solution for interfacial polymerization.
[c] Not used.

fruits, and they are also commercially available with low cost. Natural polyphenols have been widely studied and used as surface modification materials due to their unique properties such as good adhesion, coordination with metal ions, antimicrobial properties, broad chemical versatility, and radical scavenging ability [7,27–32]. In addition, wide surface engineering applications of the polyphenols are possible because they can easily adhere to various substrates by forming covalent and/or non-covalent bonding structures and be polymerized in basic conditions by self-oxidative polymerization, then uniform coating can be formed [7,28,29,32].

Herein, GO surface was modified by tannic acid (TA), one of the polyphenol derivatives, for utilizing the advantageous properties of both GO and polyphenols. The surface modified GO by TA was incorporated into the PA membrane, and the resulting membrane exhibited a significant increase in water flux, chlorine resistance, and antimicrobial properties.

2. Experimental section

2.1. Materials

Graphite kindly supplied from BASF (Germany) was used as a precursor for the preparation of graphene oxide (GO). Polysulfone (PSf) membrane was received from Woong-jin Chemicals (Republic of Korea) and used for a support membrane of the thin film composite (TFC) membranes. Sulfuric acid (H_2SO_4, 98%) and isopropyl alcohol (IPA) were received from Daejung chemicals (Republic of Korea) and used as received. *m*-Phenylenediamine (MPD, 99%), trimesoyl chloride (TMC, 98%), tannic acid (TA), Tris-buffer agents (Trizma® HCl and Trizma® base), sodium hypochlorite (NaOCl, 10–13%), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, for ESR analysis), and sodium chloride (NaCl, 99%) were purchased from Aldrich and used without any purification. Deionized (DI) water was obtained from water purification system (Synergy, Millipore, USA), having a resistivity of $18.3\ \mathrm{m\Omega\,cm}$. *n*-Hexane (95%) was received from Samchun Chemicals (Republic of Korea).

2.2. Preparation of GO and GO coated by TA (GOT)

GO was prepared through the modified Hummers method, as reported elsewhere [11,18–20]. The surface of GO was coated by TA via self-polymerization of TA. 100 mg of GO was dispersed in 200 mL of Tris-buffer solution (100 mM, pH 8.5). 200 mg of TA was dissolved in the GO-dispersed buffer solution and stirred for 24 h at room temperature. The reaction solution was diluted with 500 mL of water and filtered using anodic aluminium oxide (AAO) filter. The filtered solid (GOT) was dried in a 35 °C vacuum oven over 24 h and the product, GOT, was obtained in 82% yield.

2.3. Preparation of the polyamide membrane (PA membrane) and the polyamide membranes containing TA, GO, GOT, and the mixture of TA and GO (PA-T, PA-GO, PA-GOT, and PA-T-GO membranes)

The reverse osmosis membranes were prepared by the typical interfacial polymerization between MPD aqueous solution and TMC organic solution [3,9,11]. The following procedure was used for the preparation of polyamide membrane (PA membrane) without any ingredients such as TA, GO, and GOT. PSf support membrane was immersed in IPA for 10 min to activate pores and washed with water. The IPA-pretreated PSf membrane was placed in the water bath for 3 h to stabilize the pores. The membrane was placed into the bath with 1–3 wt% aqueous solutions of MPD for 3 h. The membrane was taken out and air bubbles and droplets of aqueous solution on the membrane surfaces were removed carefully by rolling a rubber roller. The membrane was fixed on a flat board with a silicon-rubber mold. The 0.1 wt% TMC solution (in *n*-hexane) was poured on the membrane saturated with aqueous solution. The excess TMC solution was removed after 1 min of reaction, and the membrane was placed in the 100 °C oven for 5 min for crosslinking as well as further polymerization. The resulting membrane was washed with water several times. Other membranes were prepared using the same procedure used for the PA membrane except the aqueous solution. The detailed compositions of the MPD aqueous solutions for the preparation of the other membranes used for comparative study are listed in Table 1. Another polyamide membrane was prepared using the aqueous solution containing 2 wt% of MPD, 0.5 wt% of DMSO, 2 wt% of TEA, 1 wt% of CSA, and 0.5 wt% of SDS (Table S2, Supporting information). Although the increase in membrane performances was observed from the membranes containing additives [46], we intentionally did not include any additives into the membranes in this study because our aim is to systematically observe the effects of the carbon nanomaterials such as GO and GOT in active layers on membrane performances.

2.4. Membrane filtration test

The water flux and salt rejection values of the membranes were obtained by the filtration experiments using lab-scale cross-flow RO membrane test unit [3,9,11]. The effective membrane area was $3.3 \times 6.8\ \mathrm{cm}^2$ with 0.3 cm of channel height. The 15.5 bar (225 psi) of feed pressure, the $2000\ \mathrm{mg\,L^{-1}}$ of NaCl feed solution (the conductivity of feed solution was about $3.84\ \mathrm{mS\,m^{-1}}$), and