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# Layer-by-layer self-assembly $TiO_2$ and graphene oxide on polyamide reverse osmosis membranes with improved membrane durability

Feifei Shao[a,*], Chunwei Xu[a], Wenbiao Ji[a], Hongzhou Dong[a], Qiong Sun[a], Liyan Yu[a,*], Lifeng Dong[a,b,*]

[a] *College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China*
[b] *Department of Physics, Hamline University, St. Paul 55104, USA*

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## ABSTRACT

Improving membrane durability associated with resistance to chlorine and biofouling is critical important for polyamide (PA) reverse osmosis (RO) membrane technology. Here, few-layered $TiO_2$ nanoparticles and graphene oxide (GO) were layer-by-layer self-assembled onto flat PA reverse osmosis membrane surfaces by hydrogen bonding and physical absorption to address this challenge. Contact angle testing proved that the membrane surface hydrophilicity was improved with the increase of bilayers. The modified PA membrane with bilayer number $\leq 6$ showed increased water flux. Moreover, XPS results indicated that $TiO_2$ and GO were attached to the membrane surface with good stability in our experimental conditions, and that GO nanoparticles played a part in improving chlorine resistance due to absorbing chlorine radicals. All modified PA membranes showed an anti-fouling effect and had an inhibitory effect on rejection reduction exposed to chlorine solution. For instance, the water flux of pristine membranes varied from 20.3 $l/m^2$ h to 7.5 $l/m^2$ h while the bilayer$_6$-coated membrane dropped from 23.6 to 17.9 $l/m^2$ h after UV light exposure and incubating with microbial cells for 3 d. Meanwhile, for the chlorine resistance, compared with 60% salt rejection of unmodified membrane, the bilayer$_6$-coated membrane was a more effective 75% after 20 h of chlorine exposure.

## 1. Introduction

Reverse osmosis (RO) has become a leading technology in waste water treatment, ultrapure water production, and water desalination [1]. The most commonly used commercial RO membranes are aromatic polyamide (PA) material, which is exemplified by an interfacially polymerized reaction on polysulfone ultrafiltration membranes. However, they often encounter performance attenuation because of microbial biofouling and poor chlorine resistance. Microbial biofouling remains the main reason for flux decline due to the microorganism accumulation. Poor chlorine resistance causes the rapidly failing of salt rejection and enlargement in flux upon chlorine exposure which can lead to the decrease of service life, so it is critically important to develop membranes with both antibacterial properties and good chlorine resistance.

To date, much progress has been made for PA reverse osmosis membranes on improving chlorine resistance and resolving microbial biofouling. There are several methods for membrane modification, including physical coating, chemical grafting, and ontology doping necessarily aided by research and development of new materials. Macromolecules and polymers are used as chlorine resistance modified materials for PA membrane modification [2–4]. Also, nanomaterials are promising materials for membrane modification to improve separation performance, anti-fouling, and chlorine resistance [5]. Recently, nanomaterials can be used in PA modification by chemical grafting and adsorption of opposite charges [6–8]. In other research fields, nanomaterial modifications with other materials have been reported in order to improve their certain performances. The nanomaterials mainly included carbon nanotubes [9–14], graphene [15,16] and $TiO_2$ [17,18] which were further modified with various metal oxides and sulfonated polyaniline by physical coating, meteorological chemical deposition, in situ self-assembly, or in-situ emulsion.

Titanium dioxide ($TiO_2$) has been used to solve a lot of water and air pollution problems due to its photocatalytic characteristics to degrade organic pollutants and kill bacteria [19]. On the other hand, graphene oxide (GO) is rich in carbonyl group which can make GO disperse well in water. Also, GO is used as a potential efficient antioxidant in membrane modification [20] by capturing hydroxyl radicals to improve chlorine resistance [21–23]. Self-assembly $TiO_2$ on PA membrane was prepared with good antifouling effect [24]. Our previous study [26]

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[*] Corresponding authors.
*E-mail addresses:* shaofeifei820@163.com (F. Shao), liyanyu@qust.edu.cn (L. Yu), donglifeng@qust.edu.cn, ldong03@hamline.edu (L. Dong).

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stated a simple method to prepare PA membrane with good chlorine resistance with few-layered GO as a protective layer by spin-coating on membrane surfaces. Choi et al. [7] reported that with opposite electrostatic adherence force, aminated-GO and GO were steady placed onto PA reverse osmosis membrane surface with good chlorine resistance. GO and $TiO_2$ have been reported as PA membrane modification materials [7,24], but layer-by-layer self-assembly of both $TiO_2$ and GO on polyamide reverse osmosis membranes has not been reported. The simultaneous use of $TiO_2$ and GO can improve both antibacterial properties and chlorine resistance ability. $TiO_2$ can be connected to PA membrane by forming a bidentate coordination between $Ti^{4+}$ and two oxygen atoms of −COOH group [24] or by H-bond between surface hydroxyl group of $TiO_2$ and −COOH group of the membrane surface [25]. Therefore, it is possible to use $TiO_2$ as the connection bridge to link GO and PA membrane surface in order to achieve layer-by-layer self-assembly of both $TiO_2$ and GO on polyamide membrane. This is because GO is rich in oxygen-containing groups such as −COOH to form hydrogen bonds with $TiO_2$. On the other hand, self-assembly of opposite charges on $TiO_2$ and GO may be enhanced by charge attraction. Moreover, compared to literature [7], if positively charged $TiO_2$ can replace aminated-GO to achieve self-assembly with GO, it will be cost saving because the preparation of $TiO_2$ is relatively cheaper compared with that of aminated-GO. Meanwhile, it can make the membrane have both resistances to chlorine and antimicrobial properties.

In this study, we achieved layer-by-layer (LbL) self-assembly of $TiO_2$ and GO nanoparticles onto PA flat membrane surfaces by H-bond and physical absorption. Firstly, $TiO_2$ nanoparticles self-assembled onto PA membrane by an H-bond between carbonyl group and surface hydroxyl group of $TiO_2$. Secondly, hydroxyl group of $TiO_2$ connected oxygen-containing groups such as carbonyl group of GO with H-bond. Finally, the modified membrane was prepared. Relative to our previous research [26], adsorption coating was relatively stable compared to physical adsorption; on the other hand, $TiO_2$ are sterile compared to GO. Contact angle testing proved that the hydrophilicity of membrane surface was improved with the layer number increased. Both water flux and salt rejection of modified membrane increased with layer number ≤ 6. Moreover, XPS results indicate that $TiO_2$ and GO were attached to the membrane surface with good stability in our experimental conditions, and that GO nanoparticles played a part in improving chlorine resistance due to absorbing chlorine radicals. All modified membranes showed an anti-fouling effect and an inhibitory effect on rejection reduction exposed to chlorine solution. For instance, the water flux of pristine membranes varied from 20.3 $l/m^2$ h to 7.5 $l/m^2$ h while that of the $bilayer_6$-coated membrane dropped to 17.9 $l/m^2$ h with UV light after exposure to microbial cells for 3 days. Meanwhile, for the chlorine resistance, compared with 60% salt rejection of unmodified membrane, the $bilayer_6$-coated membrane was a more effective 70.8% after 16 h of chlorine exposure.

## 2. Materials and chemicals

Polysulfone flat membrane has molecular weight cut-off at 30,000. All chemicals, if not otherwise specified, were obtained from Aladdin Corp. (Shanghai, China): graphene oxide powder (G139803), sodium chloride (NaCl), titanium dioxide ($TiO_2$, the particle size is around 100 nm, as shown in Fig. S1 in the supplementary information (SI)), sodium hydroxide (NaOH), n-hexane, isopropyl alcohol, sodium hypochlorite (NaOCl, 10% aq.), 1,3,5-benzenetricarbonyl chloride (TMC, > 98%), and *m*-phenylenediamine (MPD, > 99%).

### 2.1. Characterization of nanosheets and membranes

Fourier transform infrared (FT-IR, Nicolet iN10, Thermo) spectrum was obtained to test functional groups of membrane surfaces. A goniometer (3250-DS3210, Germany) was used to measure water contact angles of membrane surfaces. Transmission electron microscope (TEM, JEM-1011, JEOL) and scanning electron microscope (SEM, HItachi-s-4800) were performed to observe surface morphology and the dimension of GO and $TiO_2$. X-ray photoelectron spectroscopy (XPS) was performed using a twin-anode Al Kα (1486.6 eV) X-ray source within the range from 0 to 1400 eV. The difference of element type and chemical bonds between pristine and modified membranes can help to indicate whether $TiO_2$ and GO were adhered onto the membrane surface. Moreover, the bonding chemistry can help to research the chlorine resistance principle of the coating layers on PA membrane surface.

### 2.2. The preparation of PA reverse osmosis membrane

The flat PA composite membranes were fabricated by the interfacial polymerization reaction on the polysulfone membrane top surface. Specifically, the polysulfone membrane was rinsed with isopropyl alcohol to remove any preservatives and then washed thoroughly with pure water. After that, the MPD (2 wt%) aqueous solution was poured onto the top surface of the polysulfone flat membrane for 1 min. It is important to blow off any redundant droplets of the amine solution on the polysulfone surface. After that the interfacial polymerization reaction was induced by bringing TMC in hexane solution (0.1 wt%) into contact with membrane surface for 40 s. The excess organic solution on the membrane surface was removed, and the resulting PA membranes were dried at 60 °C for 10 min. At last the prepared membranes were washed and stored in water.

### 2.3. Modification of PA membrane with $TiO_2$/GO layers

Firstly, $TiO_2$ and GO nanoparticles were dispersed in water, both with concentrations of 0.005 mg/ml, by ultrasonic sonicating for 1 h in order to form uniform dispersion. Secondly, the neat PA membrane was dipped in the transparent $TiO_2$ colloidal solution for 1 h. Then the first layered membrane was softly washed with water to wipe off redundant solution, and particles absorbed on membrane surface by hydrogen bond were reserved and then naturally dried before coating with GO solution. Thirdly, GO was deposited onto the $TiO_2$-coated membrane surface by dipping into GO water dispersion for 1 h, then washed with water and dried in air. At last, after repeating the coating step 2 and 3 above, few-layered $TiO_2$ and GO modified PA reverse osmosis membranes were prepared.

### 2.4. Membrane separation performance

The membrane separation performance test was conducted at cross flow system under a 1.5 MPa pressure with 1 mg/ml NaCl aqueous solution. Water flux (F) and salt rejections (R) were calculated by the following two equations: $F = V/At$ and $R\ (\%) = 100 \times (1 - C_p/C_f)$. Where V, A, and t are respectively the total amount of the collected permeate, cross-sectional area and a fixed time. $C_f$ and $C_p$ are the salt concentrations of feed and permeate side measured by a conductivity meter.

### 2.5. Membrane chlorine stability tests

The membrane's degradation to free chlorine presents sharp decline in the salt rejection and significant increase in water flux, so it is important to contrast water flux and salt rejection before and after chlorine exposure in order to evaluate membrane resistance to chlorine. A commercial 10% NaOCl aqueous solution was diluted in DI water to make chlorine solution with chlorine concentration of 2 mg/ml. The membranes were immersed into NaOCl aqueous solution for 0–24 h and tested for desalination performance every two hours. After washing the immersed membranes sufficiently with distilled water, water flux and salt rejection after chlorine exposure were measured with the same NaCl concentration and water pressure. Finally, the values after exposure should compare with the corresponding value prior to chlorine