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# Modification Mechanism of Polyamide Reverse Osmosis Membrane by Persulfate: Roles of Hydroxyl and Sulfate Radicals

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► **To cite this version:**

Wei Cheng, Haodan Xu, P Wang, Lihong Wang, Anthony Szymczyk, et al.. Modification Mechanism of Polyamide Reverse Osmosis Membrane by Persulfate: Roles of Hydroxyl and Sulfate Radicals. *Environmental Science and Technology*, 2022, 56 (12), pp.8864-8874. 10.1021/acs.est.2c00952 . hal-03715433

**HAL Id: hal-03715433**

**<https://hal.science/hal-03715433>**

Submitted on 25 Jul 2024

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1 **Modification Mechanism of Polyamide Reverse Osmosis**  
2 **Membrane by Persulfate: Roles of Hydroxyl and Sulfate**  
3 **Radicals**

4  
5 Submitted to

6 Environmental Science & Technology

7  
8 April 19, 2022

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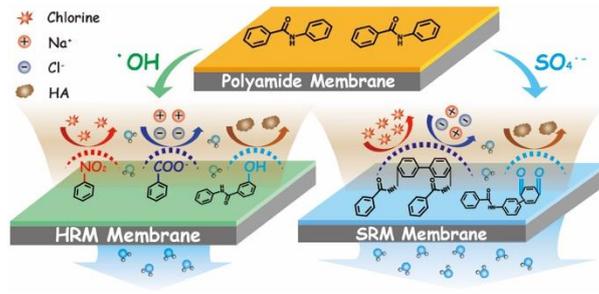
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## 31 **ABSTRACT**

32        Oxidative modification is a facile method to improve the desalination performance of thin-film  
33 composite membranes. In this study, we comparatively investigated the modification mechanisms  
34 induced by sulfate radical ( $\text{SO}_4^{\bullet-}$ ) and hydroxyl radical ( $\text{HO}^{\bullet}$ ) for polyamide reverse osmosis (RO)  
35 membrane. The  $\text{SO}_4^{\bullet-}$ - and  $\text{HO}^{\bullet}$ -based membrane modifications were manipulated by simply adjusting  
36 the pH of the thermal-activated persulfate solution. Although both of them improved water  
37 permeability of the RO membrane under certain conditions, the  $\text{SO}_4^{\bullet-}$ -modified membrane notably  
38 prevailed over the  $\text{HO}^{\bullet}$ -modified one due to higher permeability, more consistent salt rejection rates  
39 over wide pH and salinity ranges, and better stability when exposed to high doses of chlorine. The  
40 differences of the membranes modified by the two radical species probably can be related to their  
41 distinct surface properties in terms of morphology, hydrophilicity, surface charge, and chemical  
42 composition. Further identification of the transformation products of a model polyamide monomer  
43 using high-resolution mass spectrometry demonstrated that  $\text{SO}_4^{\bullet-}$  initiated polymerization reactions  
44 and produced hydroquinone/benzoquinone and poly-aromatic structures; whereas the amide group of  
45 the monomer was degraded by  $\text{HO}^{\bullet}$ , generating hydroxyl, carboxyl, and nitro groups. The results will  
46 enlighten effective ways for practical modification of polyamide RO membranes to improve  
47 desalination performances and the development of sustainable oxidation-combined membrane  
48 processes.

49 **KEYWORDS:** *polyamide RO membrane, oxidative modification, hydroxyl radical, sulfate*  
50 *radical, desalination, chlorine resistance, fouling resistance*

51 **SYNOPSIS:** Sulfate and hydroxyl radical modification of polyamide RO membrane follow distinct  
52 reaction pathways and achieve different desalination performance.

## 53 INTRODUCTION

54 Membrane technology plays an increasingly important role in desalination and water reuse to alleviate  
55 the stress of global water scarcity. Currently, reverse osmosis (RO) is leading the membrane  
56 application to augment water supply owing to its remarkable efficiency in water-solute separation and  
57 energy consumption.<sup>1, 2</sup> Across the substantial investigations on membrane materials, thin film  
58 composite (TFC) polyamide membrane, which is characterized by high water permeability, salt  
59 rejection, and chemical stability, became a gold standard for RO processes.<sup>3, 4</sup> In recent years, there  
60 are increasing demands for developing novel membranes with higher water permeability, which  
61 require less energy consumption and fewer membrane elements to be installed for brackish water  
62 desalination and wastewater reclamation.<sup>5</sup> However, inherent material limitations of the TFC  
63 membrane, such as permeability-selectivity trade-off, seriously hinder the comprehensive  
64 improvement of membrane properties.<sup>6, 7</sup> Besides, high water permeance usually aggravates  
65 membrane fouling because of the increased concentration polarization phenomenon.

66 Numerous efforts have been made to improve water permeability and fouling resistance while  
67 maintaining high solute rejection for TFC membranes. For example, incorporating nanomaterials into  
68 the membrane generates nanochannels inside the polyamide layer for fast water transport;<sup>8, 9</sup>  
69 coating/grafting hydrophilic polymers on the membrane surface produces hydrophilic hydrated shells  
70 and thus improves membrane flux and mitigates membrane fouling.<sup>10, 11</sup> However, the performance of  
71 the functionalized membranes may deteriorate due to potential release of the functional material.<sup>12, 13</sup>  
72 Post-treatment of TFC membranes with heating, alkali, or hypochlorite can significantly enhance the  
73 membrane permeance by modifying the physicochemical properties of the active layer (e.g., cross-  
74 linking degree, hydrophilicity, or thickness).<sup>14-18</sup> These simple treatments are the prevailing surface  
75 modification methods in manufacturing, although the operational conditions should be carefully

76 controlled to avoid destroying the membrane permselectivity.

77 Recently, oxidative modification with UV and persulfate has been successfully applied to  
78 improve the permeability, fouling- and chlorine-resistance of the TFC membrane.<sup>12, 19</sup> UV irradiation  
79 of the TFC membrane was delicately conducted in water.<sup>12</sup> The irradiation process breaks the cross-  
80 linked bond of polyamide to produce carboxyl and amine groups on the membrane surface, which  
81 subsequently increases membrane surface charge and hydrophilicity. Free radicals/reactive oxygen  
82 species (ROS) could be generated in the bulk solution or on the membrane surface during UV  
83 irradiation.<sup>20, 21</sup> Therefore, there are uncertainties about their functions on membrane properties. Bing  
84 et al. used heated persulfate solution at pH 8 to modify the polyamide membrane.<sup>19</sup> They proposed  
85 that hydroxyl radical (HO<sup>•</sup>) can modify the TFC membrane via surficial oxidation and interfacial  
86 crosslinking, which improves membrane permeability and chlorine resistance. Nevertheless, the  
87 speciation of radicals in the persulfate solution is pH dependent. It is well known that sulfate radical  
88 (SO<sub>4</sub><sup>•-</sup>) is generated through persulfate decomposition and can convert to HO<sup>•</sup> in reaction with OH<sup>-</sup>.<sup>22,</sup>  
89 <sup>23</sup> SO<sub>4</sub><sup>•-</sup> and HO<sup>•</sup> coexist at near-neutral pH.<sup>22, 23</sup> It is known that the two radical species have distinct  
90 reaction pathways towards some organic compounds.<sup>22, 24</sup> Their reactions with surface moieties of the  
91 polyamide membrane could be also different. Understanding the fundamental roles played by specific  
92 oxidative species will elucidate the intrinsic correlation of membrane performance and material  
93 properties and facilitate the development of high-performance TFC membranes.<sup>4</sup>

94 HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> are the most referred strong oxidants with reducing potentials of 1.90–2.70 and  
95 2.5–3.1 V, respectively.<sup>24</sup> Generally, HO<sup>•</sup> prefers to undergo hydrogen abstraction or radical addition  
96 with a broad range of organics, while SO<sub>4</sub><sup>•-</sup> is more prone to electron transfer reactions with higher  
97 selectivity towards specific functional groups.<sup>22, 24</sup> We hypothesize that HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> could react  
98 differently with polyamide polymer, considering that the polymer has both unsaturated aromatic  
99 moieties and reactive amide groups. Besides, oxidation processes such as H<sub>2</sub>O<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub>, and

100 persulfate have been investigated recently in conjunction with membrane filtration processes to  
101 mitigate membrane fouling or remove contaminants.<sup>25-27</sup> Catalytic-functionalized TFC membranes  
102 were also prepared to alleviate biofouling by in-situ generation of HO<sup>•</sup>.<sup>28, 29</sup> The emergence of these  
103 oxidation-combined membrane processes addresses the need for a better understanding of the  
104 reactions between oxidative species and polyamide membranes.<sup>30, 31</sup>

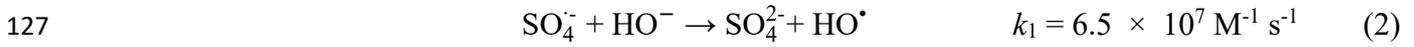
105 This study aims to compare the effectiveness of HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> for polyamide RO membrane  
106 modification and relate the differences to their reaction pathways. By simply adjusting the pH of  
107 persulfate solution in thermal activation, the predominance of HO<sup>•</sup>- or SO<sub>4</sub><sup>•-</sup>-modification was  
108 manipulated. The effects of modification by the two radicals were comprehensively compared in  
109 aspects of water permeability, chlorine- and fouling-resistance as well as solute rejection. To  
110 understand the membrane modification mechanism of the two radical species, their reactions with  
111 benzanilide (BA), a model polyamide monomer, were also investigated. The reaction pathways were  
112 proposed based on transformation product analysis using a quadrupole time-of-flight (QToF) mass  
113 spectrometer.

## 114 **MATERIALS AND METHODS**

115 **Membrane and Chemicals.** Commercial polyamide RO membranes (SW30XLE and  
116 BW30) were purchased from Dow Filmtec<sup>TM</sup>. Sodium peroxodisulfate (PDS, Sigma-Aldrich) was  
117 used as a precursor to generate radical species in solution for membrane modification. Solution pH  
118 was adjusted with dilute H<sub>2</sub>SO<sub>4</sub> or NaOH. NaCl was purchased from Aladdin (Shanghai, China).  
119 Sodium hypochlorite was supplied by Shanghai Hushi Reagent. Benzanilide (BA) and humic acid  
120 (HA) obtained from Sigma-Aldrich were used as polyamide monomer and model foulant, respectively.

121 **Oxidation Modification.** Thermal activation of PDS at pH 4 and pH 10 was used to induce  
122 SO<sub>4</sub><sup>•-</sup> or HO<sup>•</sup> generation because of the following considerations. First, PDS can be activated by heat

123 according to eq (1).  $\text{SO}_4^{\bullet-}$  generated can convert to  $\text{HO}^\bullet$  under base condition through eq (2). It was  
124 also reported that  $\text{SO}_4^{\bullet-}$  directly reacts with water to produce  $\text{HO}^\bullet$  (eq (3)). However, the reaction rate  
125 of eq (3) is very low, meaning that  $\text{SO}_4^{\bullet-}$  dominates at  $\text{pH} \leq 7$ .<sup>22</sup>



129 Also, the predominance of  $\text{SO}_4^{\bullet-}$  at pH 4 and the generation of  $\text{HO}^\bullet$  at pH 10 were further confirmed  
130 with a probe compound (i.e., 2,4-dichlorophenol) (Figure S1, SI). Second, the decomposition rate of  
131 PDS is independent of its initial concentration and remains to be constant at pH 4 and pH 10 (Figure  
132 S2a, SI).<sup>32</sup> During the membrane modification in this study (i.e., 5 h), the PDS decomposed by ~5%,  
133 which means that the PDS concentration is relatively constant. In comparison, peroxymonosulfate  
134 (PMS)/ $\text{Co}^{2+}$ , another typical process of  $\text{SO}_4^{\bullet-}$  generation, induces rapid PMS decomposition (Figure  
135 S2b, SI). The persistence of PDS during thermal activation guarantees interaction of the membrane  
136 with oxidant species at relatively constant concentrations. Third, the thermal activation of PDS can  
137 avoid the impacts of metals and UV irradiation on membrane modification. The influencing factors  
138 (i.e., PDS, pH, and heating) on membrane water flux and salt rejection were also tested individually,  
139 and negligible impacts of them on membrane performance were observed (Figure S3, SI).

140 Before modification, the membrane was immersed in isopropanol solution (25 %) for 30 min and  
141 washed thoroughly using pure water. Hydroxyl radical modified (HRM) and sulfate radical modified  
142 (SRM) membranes were fabricated by immersing the pristine RO membrane in PDS solution for 5 h  
143 at 50 °C under base (pH 10) or acidic (pH 4) conditions, which enables controlled  $\text{HO}^\bullet$  or  $\text{SO}_4^{\bullet-}$   
144 generation. It should be noted that  $\text{SO}_4^{\bullet-}$  may not completely transfer to  $\text{HO}^\bullet$  at pH 10, although the  
145 membrane property variation is mainly caused by the  $\text{HO}^\bullet$  oxidation, which will be discussed in this  
146 study. Borate buffer (5 mM) was applied for pH 10. No buffer was used for pH 4 because the solution

147 pH nearly did not change during the membrane modification. After modification, the HRM and SRM  
148 membranes were thoroughly rinsed with pure water and stored at 4 °C before use. The concentration  
149 of PDS in the solution was measured with a potassium iodide colorimetric method.<sup>33</sup>

150 **Membrane Performance Test.** Water flux and salt rejection of the pristine and modified  
151 RO membranes were measured with a bench-scale crossflow filtration system. The surface area of the  
152 membrane was 14.6 cm<sup>2</sup>. The crossflow velocity was 71.8 cm/s and the water temperature was  
153 maintained at 25 ± 0.5 °C. The water flux of RO was measured at 14 bar. Solute rejection was tested  
154 with synthetic water containing 10 mM NaCl. Humic acid was used as the model foulant to evaluate  
155 the fouling propensity of membranes at pH 7.5 before and after oxidative modification. Detailed  
156 information on the membrane performance test and fouling experiment was described in Text S1, SI.

157 **Membrane Characterization.** Surface morphology and roughness of the pristine and  
158 modified membranes were characterized by cold field emission scanning electron microscopy (FE-  
159 SEM, Hitachi SU8010) and atomic force microscopy (AFM, Bruker FastScan Bio). Surface chemical  
160 information of the membranes was analyzed with an infrared spectrometer equipped with an attenuated  
161 total reflection accessory (ATR-FTIR, Nicolet iN10MX) and an X-ray photoelectron spectrometer  
162 (XPS, Escalab 250Xi). Membrane surface charge at different pH (measuring solution: 1 mM KCl) was  
163 measured with a streaming current analyzer (Anton Paar, SurPASS 3). Contact angle of the membrane  
164 was determined using an optical goniometer (Data Physics Instruments, OCA20). Surface density of  
165 carboxyl groups on the membrane surface was quantified with a silver binding method as described in  
166 previous studies.<sup>34, 35</sup> The effective pore size of the membrane was estimated according to a pore  
167 transport model utilizing the rejection of reference organic tracers.<sup>36</sup> More details of carboxyl group  
168 areal density and pore size measurements are provided in [Text S2 and S3, SI](#).

169 **Reaction of Benzanilide Monomer and Analytical Methods.** The reaction  
170 mechanism of the polyamide membrane with oxidative species in PDS solution at different pH was

171 investigated by using BA as a model polyamide monomer. The BA monomer was dissolved in  
172 acetonitrile with a concentration of 50 mM and stored at -20 °C. Various concentrations of PDS (600,  
173 1000, and 2000 µM) were used to react with BA (200 µM) at molar ratios of 3:1, 5:1, and 10:1,  
174 respectively, at 50 °C. The pH of the PDS solution was maintained at 10 or ~4 with or without borate  
175 buffer. Samples were withdrawn at different time intervals and quenched by quick cooling down to  
176 room temperature. The concentration of BA was determined with an HPLC (Waters 2487) equipped  
177 with a Phenomenex Luna C18 column (4.6 mm × 150 mm × 5 µm) using isocratic ultrapure water and  
178 methanol (50%:50%, v/v) of 1 mL min<sup>-1</sup> as mobile phase and detection wavelength of 260 nm. BA  
179 transformation products were analyzed using a QToF mass spectrometer (X500R, AB SCIEX) operated  
180 in the negative (for samples reacted at pH 10) or positive (for samples reacted at pH 4) IDA mode.  
181 Accurate mass and empirical formulas of the degradation products were provided by the QToF.  
182 Detailed LC and MS settings are described in [Text S4, SI](#). The products were also derivatized with  
183 methanol at acid pH for GC/MS analysis. The derivatization method and the GC/MS operating  
184 condition are shown in [Text S5, SI](#).

## 185 **RESULTS AND DISCUSSION**

186 **Water Permeability and Salt Rejection of Modified Polyamide Membranes.** Water flux  
187 and salt rejection of the polyamide membrane before and after oxidative modification were measured  
188 with a crossflow RO system. The water fluxes of SRM and HRM membranes were normalized to that  
189 of the pristine membrane to clearly present the effect of oxidative modification on the membrane  
190 permeability. Oxidative modification of the SW30 membrane under acidic or base conditions  
191 significantly improved its water permeability, with higher fluxes being observed under larger PDS  
192 doses ([Figure 1](#)). For example, the water permeability of SRM<sup>SW30</sup> and HRM<sup>SW30</sup> membranes were  
193 ~270% and ~190% higher than the pristine SW30 membrane, respectively, after modification at the

194 PDS dose of 35 g/L. In contrast to the water permeance, radical exposures have a minimal influence  
195 on NaCl rejection until the PDS doses increased to 50 g/L. Under this condition, the NaCl rejection  
196 decreased to 85.0% and 90.9% for the SRM and HRM membranes, respectively. The results suggest  
197 that the oxidative modification at moderate PDS doses can effectively improve the water permeance  
198 of the polyamide membrane while maintaining high salt rejection.

199 Interestingly, the modification at pH 4 (SRM<sup>SW30</sup>) achieved higher efficiency (i.e., a lower PDS  
200 dose is needed to achieve equal improvement of water permeability) than that at pH 10 (HRM<sup>SW30</sup>).  
201 The water permeability increment of the polyamide membrane exerted by PDS modification showed  
202 an obvious threshold of PDS dose (i.e., ~10 g/L) at pH 10. In contrast, the water permeability was  
203 more sensitive to the PDS dose when the membrane was modified at pH 4. In other words, the  
204 polyamide membrane exhibits different reactivity towards the oxidant species generated at pH 4 and  
205 10. Also, the surface color of the SRM<sup>SW30</sup> membrane was quite different from the HRM<sup>SW30</sup> (Figure  
206 S4, SI). These results imply that the modification mechanism at the two pH values might be different,  
207 and may influence the membrane performance in different ways which is the focus of this study.

208

### Figure 1

209 **Surface Characterization of the Modified Membranes.** The surface morphology of the  
210 pristine and modified SW30 membranes was visualized by SEM and AFM. The oxidative  
211 modification was conducted with 4 g/L PDS at pH 4 or 30 g/L PDS at pH 10 to obtain the SRM<sup>SW30</sup>  
212 and HRM<sup>SW30</sup> membranes, respectively, having comparable water flux and salt rejection. The  
213 SRM<sup>SW30</sup> membrane showed a similar ridge-and-valley structure to the pristine membrane, while this  
214 structure slightly dimed and the thickness of the active layer decreased for the HRM<sup>SW30</sup> membrane  
215 (Figures 2a–c and S5) implying degradation of the polyamide layer. This result is consistent with the  
216 lower roughness of the HRM<sup>SW30</sup> membrane ( $R_q = 68.45$  nm) than the SRM<sup>SW30</sup> ( $R_q = 76.80$  nm). The  
217 morphological difference between the HRM<sup>SW30</sup> and SRM<sup>SW30</sup> membranes seems contradictory to the

218 difference in their water permeability (Figure 1). We suppose that the change in the material  
219 physicochemical properties may play an important role in the filtration performance of the modified  
220 membranes.

## 221 **Figure 2**

222 ATR-FTIR spectra of the pristine and modified SW30 membranes are presented in Figure S6 (SI).

223 Both polyamide and polysulfone layers showed characteristic peaks in the 1000–1800  $\text{cm}^{-1}$  range

224 (Figure S6a, SI).<sup>37</sup> Typical peaks that can be assigned to polysulfone include: i) 1584, 1504, and 1487

225  $\text{cm}^{-1}$  (aromatic ring), ii) 1411, 1387, 1363  $\text{cm}^{-1}$  (C-H moiety), iii) 1322, 1294, 1169, 1148  $\text{cm}^{-1}$  ( $\text{SO}_2$

226 moiety), and iv) 1239  $\text{cm}^{-1}$  (C-O-C moiety).<sup>38</sup> The IR bands of polysulfone before and after

227 modification are quite similar, which implies that the oxidative modification employed in this study

228 has minimal impact on the polysulfone supporting layer. The spectrum recorded for the aromatic

229 polyamide layer presented 3 typical amide bands, i.e., the amide I at 1669  $\text{cm}^{-1}$  (C=O stretching), the

230 aromatic amide at 1609  $\text{cm}^{-1}$  (N-H or C=C ring vibration), and the amide II at 1541  $\text{cm}^{-1}$  (N-H in-

231 plane bending and N-C stretching vibration). The spectrum of the HRM<sup>SW30</sup> membrane exhibited

232 slightly lower intensity for all the 3 amide peaks, while only aromatic amide and amide II bands

233 attenuated slightly for the SRM<sup>SW30</sup> membrane. In addition, the characteristic peak of hydroxyl moiety

234 of the residual carboxyl groups at 3380  $\text{cm}^{-1}$ <sup>39,40</sup> became broader for the HRM<sup>SW30</sup> membrane (Figure

235 S6b, SI), implying that the decomposition of amide may produce extra carboxyl groups.

236 XPS high-resolution scans of C 1s, O 1s, and N 1s can provide additional information on the

237 polyamide layer of the pristine and modified SW30 membranes (Figures 2d, 2e, and S7). Negligible

238 changes of C-C (248.8 eV), C-N or C-OH (286.1 eV), and C=O vibration of amide (288.1 eV) were

239 observed for the SRM<sup>SW30</sup> membrane.<sup>12, 41</sup> However, a peak assignable to the  $\pi \rightarrow \pi^*$  shake-up

240 satellite emerged at 291.4 eV (the inset in Figure 2d). It is likely due to the formation of polycyclic

241 aromatic structures, such as biphenyl or multi-phenyls,<sup>42, 43</sup> indicating that  $\text{SO}_4^{\cdot-}$  generated from PDS

242 decomposition at the acidic pH may induce polymerization of aromatic rings on the polyamide surface.  
243 In contrast, the C-O peak at 286.1 eV shifted to lower binding energy ( $\delta_{BE} = 0.25$  eV) with higher  
244 intensity for the HRM<sup>SW30</sup> membrane. The O 1s spectrum of the HRM<sup>SW30</sup> membrane also showed  
245 higher intensity of C-O at 532.7 eV as compared with the pristine membrane (Figure 2e). These results  
246 further confirm the oxidative decomposition of the polyamide layer in the basic PDS solution. The N  
247 1s spectrum of the pristine SW30 membrane before and after modification did not show any significant  
248 difference (Figure S7, SI).

249 Surface elemental composition of the membranes was analyzed with XPS (Table S1, SI). The  
250 larger O/N ratio (2.532) of the HRM<sup>SW30</sup> membrane compared with the pristine (1.490) and the  
251 SRM<sup>SW30</sup> (1.489) indicates the generation of excess oxygenous groups and/or the cleavage of amide  
252 bond forming -COO moieties in the active layer. The more oxygenous groups and/or decreased cross-  
253 linking degree of the HRM<sup>SW30</sup> membrane are likely responsible for its enhanced water permeability  
254 and high NaCl rejection (Figure 1). Additionally, the significantly lower surface water contact angle  
255 (Figure S8, SI) and more negative surface charge (Figure S9, SI) observed for the HRM<sup>SW30</sup> should  
256 also be ascribed to the oxidation. The elemental composition of the SRM<sup>SW30</sup> membrane remained  
257 unchanged and the water contact angle and surface charge slightly decreased as compared with the  
258 pristine membrane. The difference in surface property of the HRM<sup>SW30</sup> and SRM<sup>SW30</sup> membranes  
259 implies different reactivity of HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> with polyamide, which will be addressed in the next  
260 section.

261 **Reaction of Radicals with Model Polyamide Monomer.** Benzanilide (BA) has a similar  
262 chemical structure to the primary moiety of polyamide and has been widely used as a molecular  
263 polyamide model monomer to study the reactivity of polyamide with oxidants (e.g., free chlorine) in  
264 the literature.<sup>44, 45</sup> It was selected here to investigate the reaction mechanism between polyamide and  
265 oxidant species generated in the PDS solution. Initially, experiments were conducted at pH 4 and 10

266 under PDS/BA molar ratios of 3:1, 5:1, and 10:1, respectively (Figure 3a and 3b). Hydrolysis of BA  
267 was not observed at the two pHs. PDS at room temperature was unreactive towards BA in water  
268 (Figure S10, SI). BA clearly reacted with the oxidant species generated from PDS decomposition at  
269 pH 4 and 10, and the reaction rate accelerated with increasing PDS dosage. BA degraded continuously  
270 with time at pH 4 and disappeared in 24 h at the PDS/BA molar ratio of 10:1. In contrast, only 42%  
271 BA degraded at pH 10 at the same PDS dosage and reaction time. Even when the reaction was extended  
272 to 48 h, 51% BA was still detected as residual at pH 10. The PDS decomposed at the two pHs were  
273 48.6% and 49.7%, respectively, after 48 h reaction. The lower BA degradation rate at pH 10 probably  
274 is due to the competitive consumption of HO<sup>•</sup> by BA transformation products. The relatively fast and  
275 continuous BA removal at pH 4 demonstrates higher selectivity of SO<sub>4</sub><sup>•-</sup> than HO<sup>•</sup> in reaction with BA.  
276 The different selectivity of the two radicals was also observed in the degradation of some water  
277 pollutants.<sup>46</sup> This result is consistent with the stronger PDS dosage-relevance of the membrane  
278 modification at pH 4 than that at pH 10 (Figure 1). After reaction at pH 4, clustered aggregates were  
279 generated in the BA solution, which is distinct from the transparent solution observed after the reaction  
280 at pH 10 (photos in Figure 3a and 3b). These results clearly show that reactions that dominated BA  
281 degradation at pH 4 and 10 are different.

### 282 **Figure 3**

283 The formula and plausible molecular structures of BA transformation products are provided in  
284 Figures S11 and S12 (SI) and summarized in Tables S2 and S3 (SI). At pH 4, benzamide, diphenol-  
285 BA, and benzoquinone-BA biphenyl were detected after oxidation at the PDS/BA molar ratio of 5:1.  
286 In fact, under the SO<sub>4</sub><sup>•-</sup>-dominated reaction condition, aromatic radical cations such as BA<sup>•+</sup> and  
287 benzene<sup>•+</sup> may form via electron abstraction, followed by a rearrangement to undergo side-chain  
288 oxidation, resulting in the conversion to phenols or biphenyls.<sup>24,47</sup> Then, the phenols undergo oxidative  
289 polymerization with BA<sup>•+</sup> to form oligomers.<sup>48-50</sup> As the PDS/BA molar ratio was raised to 10:1,

290 isomers of BA dimers were detected, which are characteristic products in  $\text{SO}_4^{\cdot-}$  oxidation.<sup>24</sup>  
291 Additionally, the aggregates formed under pH 4 were collected through centrifugation and  
292 characterized with FTIR (Figure S13, SI). The characteristic peaks of amide, i.e., N-H at  $3344\text{ cm}^{-1}$ ,  
293 C=O (amide I) at  $1655\text{ cm}^{-1}$ , and N-H (amide II) at  $1533\text{ cm}^{-1}$ , were consistent with those of the BA  
294 monomer. The multiple peaks of aromatic rings at the wavenumber of  $1250\text{--}1600\text{ cm}^{-1}$  merged into  
295 wider ones after reaction, which could be ascribed to the polymerization of BA and agrees with the  
296 emergence of  $\pi \rightarrow \pi^*$  satellite peak observed in the C 1s XPS spectrum (Figure 2d). The intense peak  
297 at  $817\text{ cm}^{-1}$  comes from the para-orientation of aromatic rings,<sup>51, 52</sup> indicating that the oxidative  
298 polymerization of BA forms mainly through para-substitution.

299 Oxidative hydroxylation of BA was the major reaction occurring at pH 10 at the PDS/BA molar  
300 ratio of 5:1.<sup>24</sup> Further increasing the ratio to 10:1, BA transformation products were merely detected  
301 by QToF, suggesting that the hydroxylated transformation products further degraded into small  
302 molecules. Then, the products were derivatized with methanol under acidic conditions and analyzed  
303 with GC/MS (Figure S14 and Table S4, SI). Benzoic acid and nitrobenzene were consequently  
304 detected. Nitrobenzene could be the oxidation product of aniline by  $\text{HO}^{\cdot}$  in the thermal activated PDS  
305 solution.<sup>53</sup> This result suggests that  $\text{HO}^{\cdot}$  oxidation possibly induced the cleavage of the amide bond  
306 (N-CO) of BA. Whereas for the  $\text{SO}_4^{\cdot-}$ -dominated oxidation at pH 4, neither aniline nor nitrobenzene  
307 was detected. BA dimer and benzoquinone, the characteristic transformation products observed at pH  
308 4, were not detected after the oxidation at pH 10. Plausible reaction pathways of the BA monomer  
309 under thermal-activated PDS at pH 4 and 10 are proposed in Figure 3c. Based on the transformation  
310 product identification and the one order of magnitude higher reaction rate constant of  $\text{HO}^{\cdot}$  with  
311 benzamide than that of  $\text{SO}_4^{\cdot-}$  ( $2.6 \times 10^9\text{ M}^{-1}\text{s}^{-1}$  vs.  $1.9 \times 10^8\text{ M}^{-1}\text{s}^{-1}$ )<sup>54</sup>, we can conclude that the  
312 reaction of BA was governed by  $\text{HO}^{\cdot}$  and  $\text{SO}_4^{\cdot-}$ , respectively, at pH 10 and 4. In addition, even  $\text{SO}_4^{\cdot-}$   
313 exists at pH 10, its interaction with polyamide membrane (with  $\text{p}K_{\text{a}} \sim 5.2$ <sup>55</sup>) is not favorable due to

314 electrostatic repulsion. The swelling behavior of polyamide at pH 10 due to the increased electrostatic  
315 repulsion between the dissociated carboxylic groups may increase the interaction of radicals.<sup>56</sup> Besides,  
316 the reaction rate constants of HO<sup>•</sup> towards aniline ( $1.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ ) and benzoic acid ( $4.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ),  
317 the ionized moieties in the polyamide layer, are higher than those of SO<sub>4</sub><sup>•-</sup> ( $7.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  and  
318  $1.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ).<sup>22, 57, 58</sup> However, the modification was more effective at pH 4 than pH 10 (Figure 1).  
319 It is consistent with the reaction rates of SO<sub>4</sub><sup>•-</sup> and HO<sup>•</sup> with BA, the primary moiety in the polyamide  
320 layer (Figures 3a and 3b). Hence, we can speculate that the major modification reaction occurred  
321 between radicals and the BA moiety, which presents minor changes in speciation in the pH range of  
322 4–10 ( $\text{p}K_{\text{a}} = 16.53$ )<sup>59</sup>. Therefore, the differences in the physicochemical property, as well as the  
323 filtration performance of the HRM<sup>SW30</sup> and SRM<sup>SW30</sup> membranes, can be ascribed to the different  
324 reaction pathways of HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> towards polyamide.

325 **Correlation between Membrane Surface Property and Performance.** As discussed  
326 above, PDS thermally activated under acidic or base conditions modified the polyamide membrane  
327 through different mechanisms. The modification at pH 10 broke the amide bonds of the polyamide  
328 layer and endowed the HRM<sup>SW30</sup> membrane with excess hydroxyl, carboxyl, and nitro groups. This  
329 change of surface chemistry improved hydrophilicity (Figure S8, SI), enhanced surface charge (Figure  
330 S9, SI), and slightly increased the estimated pore size (Table S5,  $r_{\text{p}} = 0.3648 \text{ nm}$ ) as compared with  
331 the pristine SW30 membrane ( $r_{\text{p}} = 0.3504 \text{ nm}$ ), which contributed to the significant increase of water  
332 permeability of the membrane (Figure 1). The carboxyl groups on the HRM<sup>SW30</sup> membrane surface  
333 were further quantified with a silver-binding method (Table S6, SI). The carboxyl group density of the  
334 HRM<sup>SW30</sup> membrane was notably higher than the pristine and SRM<sup>SW30</sup> membrane (20.40, 11.86, and  
335 13.65 sites/nm<sup>2</sup>, respectively). The formation of nitro groups was not observed in the XPS N1s  
336 spectrum ( $\sim 406 \text{ eV}$ ) (Figure S7, SI), which is likely due to the relatively low detection depth of XPS  
337 measurement (a few nanometers). SO<sub>4</sub><sup>•-</sup> initiated the redox polymerization of polyamide associated

338 with bond cleavage (HN-ring) and the following formation of biphenyl structures, strengthening salt  
339 rejection by steric exclusion ( $r_p$ : 0.3363 vs. 0.3504 nm), thereby exhibiting high salt rejection in wide  
340 pH (pH 2–9, [Figure 4a](#) and [Table S7](#)) and salinity ([Figure S15](#)) ranges. Besides, the introduced  
341 hydroquinone structure may contribute to the improved hydrophilicity and permeability of the  
342 SRM<sup>SW30</sup> membrane ([Figures 1](#) and [S8](#)).

343

#### Figure 4

344 The improvement in surface properties such as hydrophilicity induced by hydroxyl and carboxyl  
345 groups enhanced the fouling resistance of HRM<sup>SW30</sup> and SRM<sup>SW30</sup> membranes to organic foulants (e.g.,  
346 humic substances). The water flux over time, normalized by the initial value (setting at  $20.0 \pm 0.5$  L  
347  $m^{-2} h^{-1}$  by adjusting the hydraulic pressure), is shown in [Figure 4b](#). The HRM<sup>SW30</sup> and SRM<sup>SW30</sup>  
348 membranes exhibited slightly less flux decline (~10.5%) compared to the pristine membrane (13.8%  
349 reduction) after the 12 h organic fouling experiment. Also, the permeation resistance of the membrane  
350 matrix ( $R_M$ ) and fouling layer ( $R_{HA}$ ) all decreased after modification at pH 4 or 10 ([Figure 4c](#)). The  
351 hydroxyl and carboxyl groups on the modified membrane surface favor the formation of hydration  
352 shells at the membrane/water interface, hence hindering the adsorption of HA on the membrane surface.  
353 The lower HA mass desorbed from the modified membrane surface after the fouling test further  
354 confirms that less HA was adsorbed onto the surface of the modified membranes ([Figure 4c](#)).

355 Compared with the pristine membrane, both the HRM<sup>SW30</sup> and SRM<sup>SW30</sup> membranes showed  
356 higher salt rejection after chlorine exposure at various pH ([Figure 4d](#)). The conversion of the terminal  
357  $-NH_2$  groups to  $-NO_2$  on the HRM<sup>SW30</sup> membrane transformed the electronegative nitrogen (electron-  
358 donating) to electropositive (electron-withdrawing), thus reducing the chlorination reaction of residual  
359 amino groups.<sup>60</sup> Additionally, nitro groups deactivated the aromatic rings against electrophilic  
360 chlorination, with extended Huckel atomic charge being decreased from -0.179 and -0.203 to -0.05  
361 ([Figure 5a](#)). The SRM<sup>SW30</sup> membrane possessed significantly improved salt rejection even after severe

362 chlorine exposure at pH 4. The enhanced chlorine resistance of the SRM<sup>SW30</sup> membrane may be  
363 ascribed to the synergistic effect of the denser active layer and slightly reduced charge of the aromatic  
364 ring due to the formation of biphenyl- and benzoquinone-polyamide structures (Figure 5a).

### 365 **Figure 5**

366 As illustrated in Figure 5b, the polyamide membranes modified through radical oxidation  
367 possessed characteristic functional groups (HRM: -OH, -COOH, -NO<sub>2</sub>; SRM: -OH, biphenyl- and  
368 benzoquinone-) and showed comprehensively improved performance in terms of water flux and  
369 fouling- and chlorine-resistances while maintaining high salt rejection. Considering the higher reaction  
370 selectivity (lower PDS doses), higher salt rejection over wide pH and salinity ranges, and more  
371 enhanced chlorine resistance of the SRM membrane, modification in acidic PDS solution governed  
372 by SO<sub>4</sub><sup>•-</sup> is more promising. Besides, moderate SO<sub>4</sub><sup>•-</sup>-based modification could maintain the integrity  
373 of the polyamide structure. The current study mainly focused on revealing the mechanisms of  
374 performance enhancement from the viewpoint of surface physicochemical properties. Potential  
375 variations of the structural homogeneity such as internal morphology, density, and distribution of  
376 functional groups in the active layer induced by oxidative modification may also affect the membrane  
377 performance<sup>61</sup>, which will be investigated in future studies.

### 378 **Environmental implications.**

379 This study demonstrates that radical oxidation is a facile and effective modification strategy for  
380 aromatic polyamide RO membrane. The pH of the PDS solution, which governs the speciation of  
381 radicals (HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup>), distinctly determines the modification mechanism and surface properties of  
382 the modified membranes. By incorporating hydroxyl, carboxyl, and nitro functional groups, or  
383 benzoquinone and multi-phenyl structures, the water permeability, anti-fouling, and anti-chlorine  
384 capabilities of the polyamide membrane could be significantly improved without severely sacrificing  
385 salt rejection. The chemical resistance of the HRM and SRM membranes for a 6-round alternate

386 acid/base cleaning was demonstrated in [Figure S16 \(SI\)](#) and indicated the performance stability of the  
387 oxidatively modified membranes. Additionally, the HRM and SRM membranes exhibited different  
388 NaCl rejections at various solution salinities ([Figure S15, SI](#)) due to variations in surface properties  
389 (i.e., surface charge and pore size). Specifically, the HRM membrane with increased surface charge  
390 had similar NaCl rejection with the pristine membrane at mild salinity ( $\leq 100$  mM NaCl, [Table S8,](#)  
391 [SI](#)). However, the NaCl rejection of the HRM membrane was lower than the pristine as the salinity  
392 further increased to 200 and 300 mM due to the charge screening effect. In contrast, the solution  
393 salinity had less impact on the NaCl rejection of the SRM membrane, and size exclusion was supposed  
394 to play an important role in the solute rejection. Therefore, the oxidatively modified membranes,  
395 especially the SRM membrane with significantly improved filtration performance, can be potentially  
396 applied in freshwater purification, brackish water desalination, and wastewater reuse. Besides, the  
397 oxidative modification applied in the study can also improve the water permeability of brackish water  
398 RO membrane, e.g., the BW30 membrane ([Figure S17, SI](#)). The specific surface properties induced  
399 by oxidation will expand the prospects of novel materials for energy-efficient water purification.

400 This study also provides new insights into the development of sustainable oxidation-combined  
401 membrane processes. The performance of TFC membranes will vary regarding the type and  
402 concentration of oxidants introduced. Therefore, the oxidation processes generating various reactive  
403 oxygen species (e.g.,  $\text{HO}^\bullet$  or  $\text{SO}_4^{\bullet-}$ ) should be carefully designed for target treatments. For example,  
404 for the treatment with low scaling potential such as RO for water reuse, combining  $\text{SO}_4^{\bullet-}$ -oxidation of  
405 a moderate dosage may endow the membrane with high water permeance and antifouling properties.  
406 Otherwise, the non-selective  $\text{HO}^\bullet$  may cause the failure of the TFC membrane eventually and have  
407 detrimental effects on the rejection of solutes, especially for neutral small organics. For novel  
408 catalytic/electric membrane materials and oxidation-combined membrane processes that possibly  
409 generate  $\text{HO}^\bullet$  or  $\text{SO}_4^{\bullet-}$ , the negative impacts of secondary radical species (e.g.,  $\text{Cl}^\bullet$  and  $\text{Cl}_2^{\bullet-}$ ) that

410 derived from halide ions (e.g., Cl<sup>-</sup>) in the water matrix on membrane performance should be avoided  
411 (Figure S18, SI).<sup>62</sup> Specifically, the halide ions in the presence of SO<sub>4</sub><sup>2-</sup> have more detrimental effects  
412 on the permselectivity of the TFC membrane.

## 413 ACKNOWLEDGMENTS

414 We acknowledge the support from the National Key Research and Development Program of China  
415 (grant 2021YFC3201401). We also thank for the support from the National Natural Science  
416 Foundation of China (grant 52000175).

## 417 SUPPORTING INFORMATION

418 The Supporting Information is available free of charge on the ACS Publications website.

419 Detailed information of membrane performance and fouling tests (Text S1), carboxyl group area  
420 density measurement (Text S2), effective pore size measurement (Text S3), setting for QToF mass  
421 system (Text S4), methylation and setting for GC-MS analysis (Text S5), degradation of 2,4-DCP by  
422 thermally activated PDS (Figure S1), decomposition of PDS and PMS (Figure S2), effect of  
423 background condition on RO membrane performances (Figure S3), photos of membranes (Figure S4),  
424 active layer thickness (Figure S5), ATR-FTIR spectra (Figure S6), N 1s XPS spectra (Figure S7), water  
425 contact angle (Figure S8), and surface zeta potential (Figure S9) of the membranes before and after  
426 modification, BA degradation at room temperature (Figure S10), QToF IDA survey of the BA  
427 degradation products (Figure S11), IDA TOF MSMS spectra of the BA degradation products (Figure  
428 S12), FTIR of the aggregated product (Figure S13), GC/MS analysis of the BA degradation products  
429 (Figure S14), NaCl rejection at different solution salinities (Figure S15), chemical resistance (Figure  
430 S16), modification of BW30 membranes (Figure S17), effect of halide ions (Figure S18), XPS surface  
431 elemental composition (Table S1), formula and proposed structure of the BA degradation products  
432 (Tables S2-S4), rejection of tracers and estimated average pore radius (Table S5), surface carboxyl  
433 group areal density of the membranes (Table S6), solute rejection at pH 2 and 3 (Table S7), and typical  
434 water salinity (Table S8).

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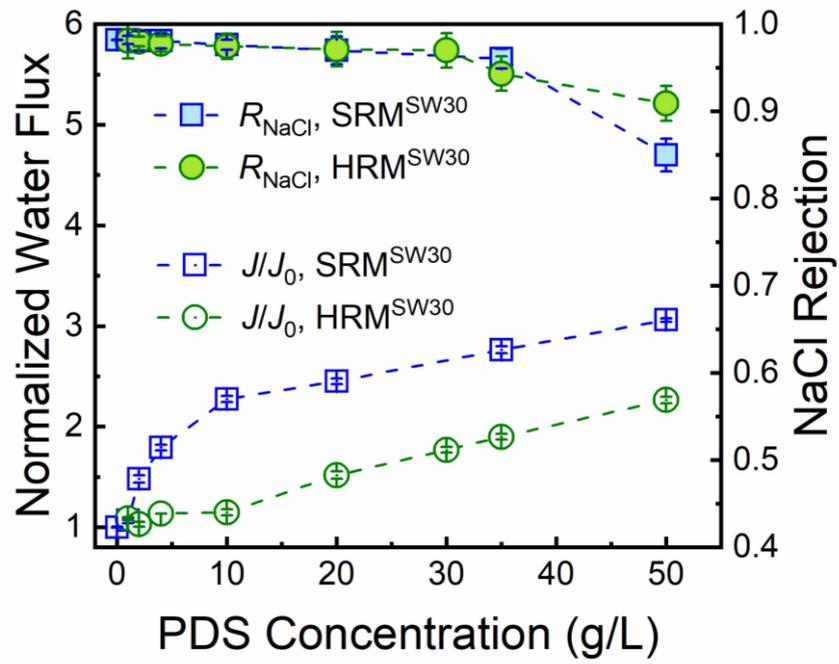
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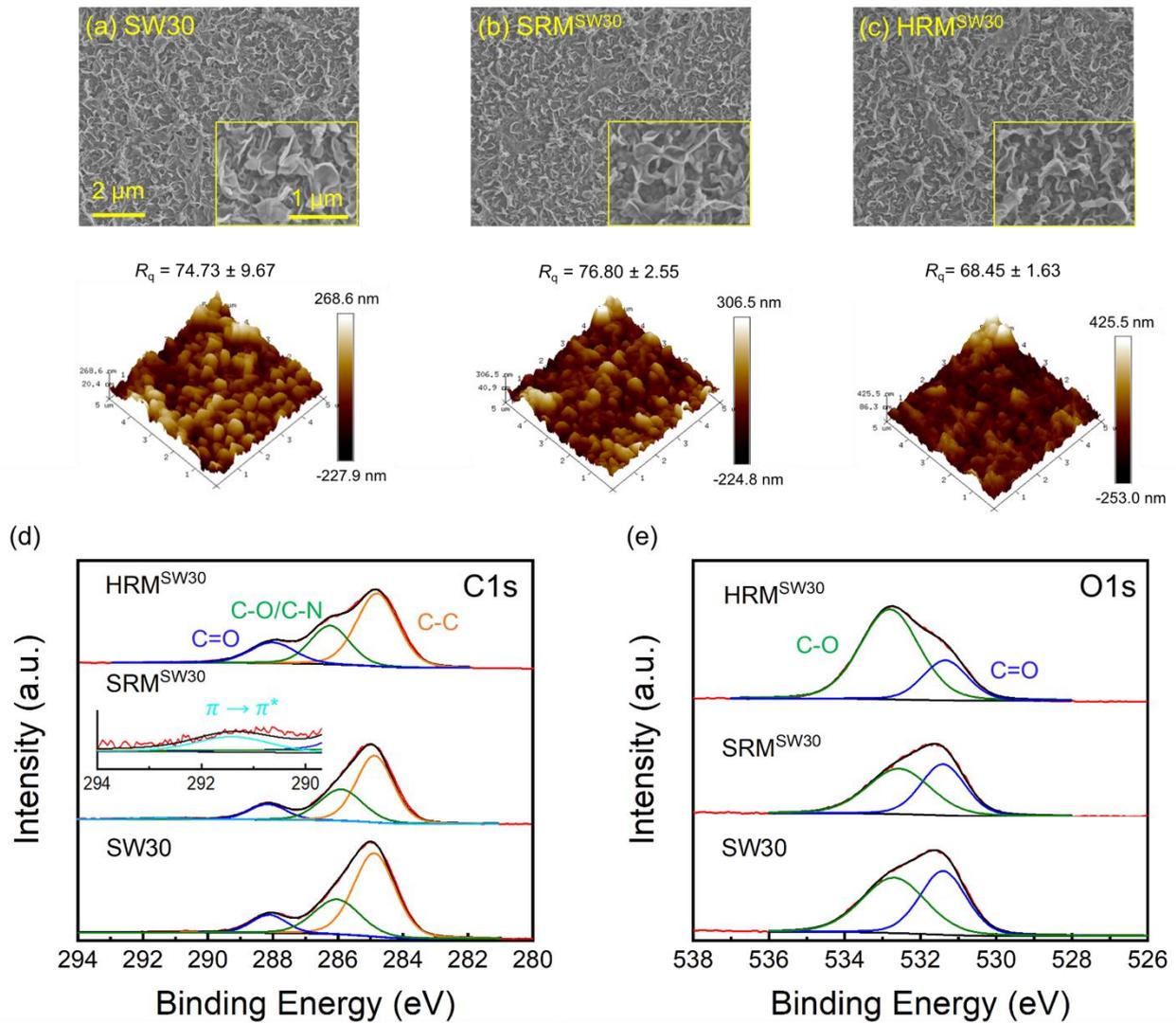
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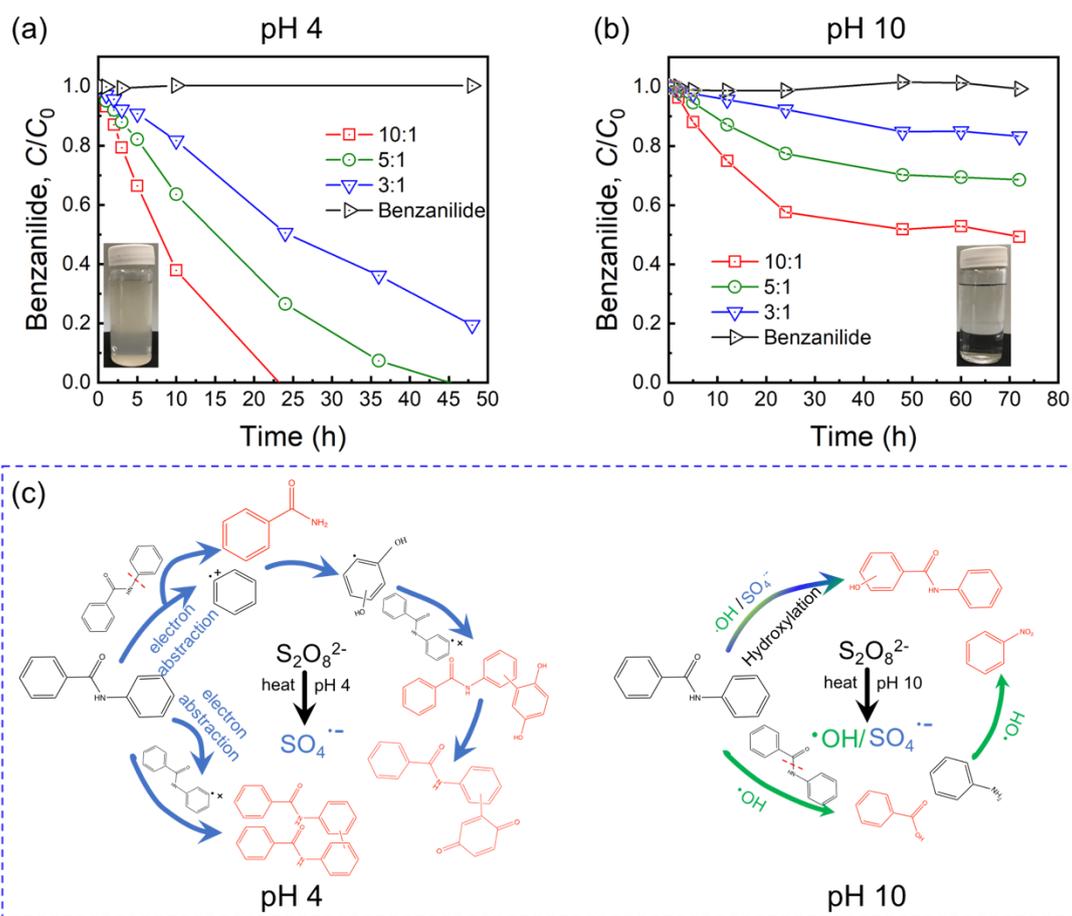
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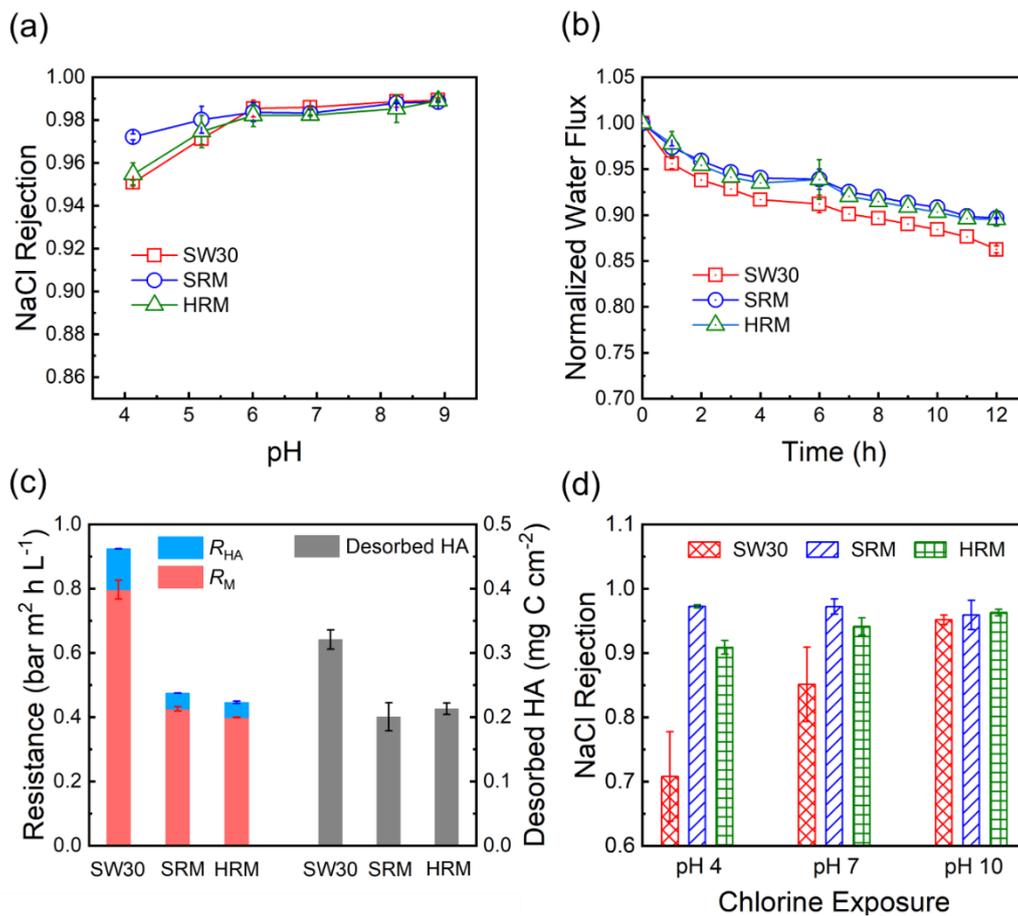
**Figure 1.** Normalized water flux and salt rejection of the polyamide SW30 membrane before and after oxidative modification. The PDS dose was 1–50 g/L for the modification of SW30. The water flux of the pristine SW30 membrane was  $17.50 \pm 0.20 \text{ L m}^{-2} \text{ h}^{-1}$  at hydraulic pressures of 14 bar.



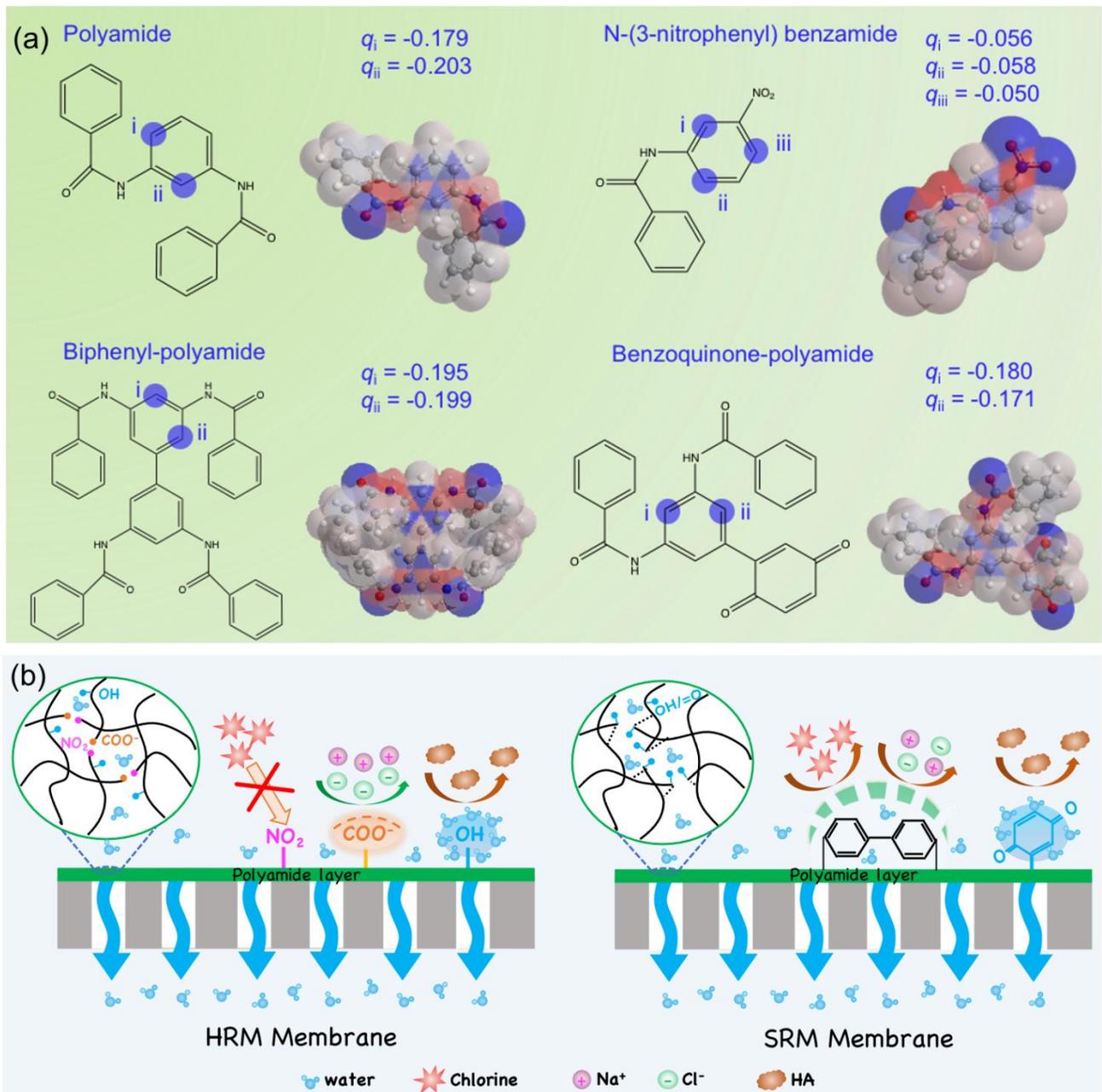
**Figure 2.** Surface characterization for the pristine and modified SW30 membranes. SEM (scale bar = 2 μm) and AFM morphologies of the SW30 (a), SRM<sup>SW30</sup> (b), and HRM<sup>SW30</sup> (c) membranes. The roughness values ( $R_q$ ) of the SRM and HRM membranes are significantly different from each other (Student's  $t$ -test,  $n = 3$ ,  $p < 0.05$ ), while the roughness of the pristine SW30 shows a relatively large deviation which may be due to samples discrepancy. XPS spectra of C1s (d) and O1s (e) for the pristine and modified SW30 membranes. The SW30 membrane was modified by using 4 g/L PDS at pH 4 (SRM<sup>SW30</sup>) or 30 g/L PDS at pH 10 (HRM<sup>SW30</sup>).



**Figure 3.** Degradation of BA monomer by PDS at pH 4 (a) and pH 10 (b). Various concentrations of PDS (600, 1000, and 2000  $\mu\text{M}$ ) were used to react with BA (200  $\mu\text{M}$ ) at molar ratios of 3:1, 5:1, and 10:1, respectively. Plausible transformation products and reaction pathways of BA with PDS at pH 4 and pH 10 (c). The proposed structures of BA transformation products were analyzed by QToF mass spectrometer and GC/MS (marked in red).



**Figure 4.** (a) NaCl rejections of the pristine and modified SW30 membranes at different solution pH (4.0–9.5). (b) Water flux variation of the membranes in the presence of HA. The initial water flux was set at  $20.0 \pm 1.0 \text{ L m}^{-2} \text{ h}^{-1}$  by adjusting the hydraulic pressure. The final water flux values of the SRM and HRM membranes are significantly different from the value of the pristine SW30 (Student's  $t$ -test,  $n = 2$ ,  $p < 0.05$ ). (c) Membrane resistance ( $R_M$ ), fouling resistance ( $R_{HA}$ ), and HA mass desorbed from the membrane surface after the fouling test. (d) NaCl rejection of the membranes having been exposed to 2000 mg/L NaOCl solution for 5 hours. The pH of the NaOCl solution was adjusted to 4, 7, or 10 with dilute HCl and NaOH.



**Figure 5.** (a) Extended Huckel atomic charge analysis of the typical moieties (polyamide structure, N-(3-nitrophenyl) benzamide, biphenyl-polyamide structure, and benzoquinone-polyamide structure) in the pristine and modified polyamide membranes. The analysis was obtained from Chem3D program (19.1 version). (b) Schematic illustration of the performance enhancement in terms of water flux, fouling- and chlorine-resistance of the hydroxyl radical-modified (HRM) and sulfate radical-modified (SRM) membranes.