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Synthesis and application in water purification**

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10

11 **Atmospheric pressure atomic layer deposition for tight ceramic nanofiltration membranes:**
12 **synthesis and application in water purification**

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22

23 **Abstract:**

24 Tight ceramic nanofiltration (NF) membranes allow efficient separation of organic
25 matter and ions for advanced water treatment. These membranes are typically
26 produced by the sol-gel method. Recently, atomic layer deposition (ALD), a self-
27 limiting gas phase coating technique, has been explored for membrane fabrication
28 and modification. In this work, the synthesis of tight ceramic NF membranes is
29 demonstrated using atmospheric pressure ALD (APALD), which is operated without a
30 vacuum-generation system compared to the commonly reported vacuum-based ALD
31 method. Titanium dioxide was coated on nano-porous membrane substrates using
32 merely one to three cycles of APALD. The average size of active pores was effectively
33 narrowed by 0.2 nm, from 0.7 nm to 0.5 nm. In addition, the size distribution of the
34 active pores became more uniform after the APALD modification. The fabricated tight
35 ceramic NF membranes had a molecular weight cut-off (MWCO) ranging from 260 to
36 380 Da while maintaining high water permeability at $11\text{-}16\text{ L m}^{-2}\text{ h}^{-1}\text{ bar}^{-1}$, which is
37 notably higher than the commercial tight polymeric NF and sol-gel-made tight
38 ceramic NF membranes. It was observed that conformal TiO_2 thin films can be
39 deposited on planar surfaces under the APALD with a growth rate of 0.39 nm per
40 cycle, while the deposition in the membrane micropores was at a lower rate,
41 estimated as 0.05 nm per cycle.

42 **Keywords:**

43 Ceramic membrane filtration; nanofiltration; atmospheric pressure atomic layer deposition;
44 water treatment

45

46 **Abbreviations**

47	AFM	atomic force microscopy
48	ALD	atomic layer deposition
49	APALD	atmospheric pressure atomic layer deposition
50	BET	Brunauer-Emmet-Teller theory
51	GPC	growth-per-cycle
52	HPLC	high performance liquid chromatography
53	MF	microfiltration
54	MW	molecular weight
55	MWCO	molecular weight cut-off
56	NF	nanofiltration
57	PEG	polyethylene glycols
58	RO	reverse osmosis
59	SEC	size exclusion chromatography
60	SEM	scanning electron microscope
61	TMP	trans-membrane pressure
62	UF	ultrafiltration

63

64 **Nomenclature**

65	$C_{i,feed}$	PEG concentration in the membrane's feed solution (-)
66	$C_{i,permeate}$	PEG concentration in the membrane's permeate solution (-)
67	d_s	molecular size of PEG tracers (nm)
68	J	membrane flux ($L\ m^{-2}\ h^{-1}$)
69	$L_{p,20^\circ C}$	membrane's water permeability at 20 °C ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)
70	ΔP	transmembrane pressure (bar)
71	R_q	root mean square roughness (nm)
72	R_a	roughness average (nm)
73	R_i	rejection rate of PEG (-)
74	S_{MW}	standard deviation of the molecular weight distribution (-)

75 T temperature of water (°C)

76

77 **Greek letters**

78 $\sigma(MW_s)$ reflection coefficient for a PEG with a molecular weight of MW_s (-)

79 η_{20} and η_T permeate viscosity at 20 °C and at the measured water temperature (Pa·s)

80

81 **1. Introduction**

82 Since the development of synthetic membranes in the 1960s, the application of membrane
83 filtration in water treatment has grown exponentially in recent decades [1-4]. Membrane
84 technology, including ultrafiltration (UF), microfiltration (MF), nanofiltration (NF) and
85 reverse osmosis (RO), has been widely deployed in drinking water purification and
86 wastewater treatment. In recent years, inorganic/ceramic UF and MF membranes have
87 gained increased attention. Although their price is higher, ceramic membranes have many
88 advantages over traditional polymeric membranes, including high mechanical strength, high
89 chemical and thermal resistance, long lifespans, and recyclability as raw ceramic material [5,
90 6].

91 An increasing number of recent studies have also focused on (hydrophilic) ceramic NF
92 membranes [5, 7-15]. The ceramic NF has been successfully used to treat various waste
93 streams in full-scale, including, among others, dye removal from textile wastewater and
94 treatment of oily wastewater [13, 16]. In our previous work, a commercial loose ceramic NF
95 membrane (450 Da, Inopor GmbH, Germany) was applied to directly filter domestic
96 wastewater for water reclamation and resource recovery [17, 18]. The tested membranes
97 showed excellent anti-fouling properties, but the rejection of dissolved organic matter and
98 ionic compounds was not satisfactory: it was lower than that of the polymeric (tighter) NF

99 membranes [17]. Therefore, a scalable tight ceramic NF membrane is expected to facilitate a
100 number of innovative applications for water reuse and wastewater treatment. Despite
101 several lab-scale studies on tight ceramic NF membranes (molecular weight cut-off (MWCO)
102 < 400 Da) [8-10, 12, 15, 19], a majority of the commercially available ceramic NF membranes
103 belong to the category of loose NF membranes (> 400 Da MWCO), with the tightest reaching
104 450 Da MWCO [7].

105 It remains a challenge to develop tight ceramic NF membranes [20], partly because they are
106 commonly made via the sol-gel method. The process involves conversion of monomers into
107 a colloidal solution (sol) that acts as the precursor for an integrated network (gel) of either
108 discrete particles (so-called particulate sol-gel route [9]) or network polymers (so-called
109 polymeric sol-gel route [12]). A major limitation of the particulate sol-gel method is the
110 resulting low permeability of the membranes: e.g. $0.5 - 1.5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for 200 Da ceramic
111 NF membranes [8, 9, 15, 19]. The low water permeability is a result of the thick coating
112 layers (up to $1 \mu\text{m}$ of dip-coated layers [15]). Using the polymeric sol-gel method, smaller
113 particles can be formed in the polymeric sol and thinner separation layers can be coated.
114 The result is improved water permeability to $2 - 4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ [10, 12], which is still lower
115 than the permeability of polymeric NF membranes.

116 The application of atomic layer deposition (ALD), a self-limiting gas phase coating technique
117 for growing atomic-scale thin films [21], has emerged as a potential route for fabrication and
118 modification of ceramic membranes [6, 22, 23]. ALD provides highly uniform and conforming
119 coating of metal oxides on 3-D structures due to alternating, self-limiting saturated surface
120 reactions. The coated layers can be deposited on the pore walls, resulting in the desired pore
121 size reduction. Li, et al. [22] firstly demonstrated the idea of using ALD to reduce the pore

122 aperture of a water permeation ceramic membrane, who succeeded in narrowing the pore
123 size of an ultrafiltration membrane from 50 nm to about 6.8 nm after deposition of alumina
124 (Al_2O_3). The water permeability of the coated membrane progressively decreased from 1698
125 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ to $118 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$. A recent study revealed that TiO_2 loose NF membranes
126 can be obtained via ALD using asymmetric substrates of 20 nm pores [23]. The coated
127 membranes showed a pore size of approximately 1 nm. Interestingly, the ALD-modified NF
128 membrane showed excellent water permeability, as high as $48 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$, which is about
129 twice as high as that of the sol-gel-made NF, as reported by Puhlfürß, et al. [7].

130 Atmospheric pressure atomic layer deposition (APALD) does not involve the use of expensive
131 vacuum-compatible equipment [21] as used in the aforementioned studies. This enables an
132 easier scale-up approach towards large-volume manufacturing. Although APALD has already
133 been demonstrated for coating (nano-)particles [24-26] and nonporous planar surfaces [27],
134 this technique has not yet been applied to deposit thin films on porous ceramic membranes.

135 In this study, we applied APALD to fabricate tight ceramic NF membranes with high water
136 permeability. The effect of APALD on the water permeability, rejection of polyethylene
137 glycols (PEGs) and the MWCO of the coated membranes was investigated. The influence of
138 APALD coating on pore size distribution is elucidated based on the Brunauer-Emmet-Teller
139 (BET) theory as well as a pore model based on the polyethylene glycols' rejection profile.

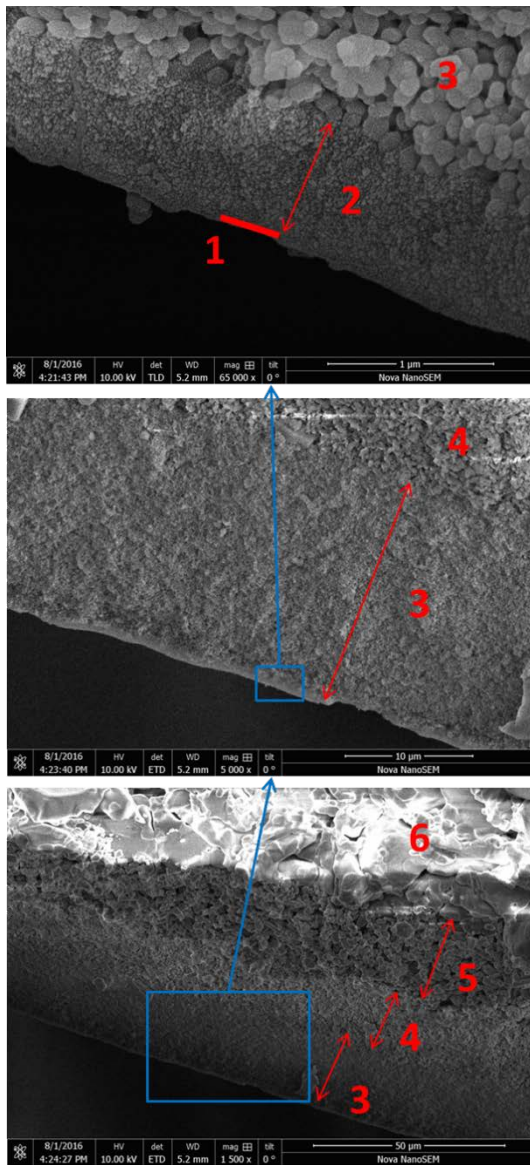
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141 **2. Materials and Methods**

142 **2.1 Substrate membranes**

143 Commercial ceramic NF membranes (Inopor GmbH, Germany) were used as the substrate
144 for APALD coating. The Inopor membrane has a single-channel tubular configuration with an
145 inner diameter of 7 mm, an outer diameter of 10 mm, a length of 100 mm) , and an effective
146 filtration area of 0.00163 m². The geometry of the membrane and calculation of the effective
147 filtration area are described in the Supplementary Material (Figure S1 and Equation S1). The
148 cross-section structure of the pristine membrane (Figure 1) was analysed using a scanning
149 electron microscope (SEM, FEI Nova NanoSEM 450, USA). The separation layer of the
150 received membrane, which is located at the inner surface of the tubular membrane, is made
151 of titanium dioxide (TiO₂) with a porosity of 30%, as described by the manufacturer, and the
152 other layers are made of alumina (Al₂O₃). These membranes have an MWCO of 450 Da as
153 claimed by the supplier. However, great variation in actual MWCO of these membranes were
154 observed, and 6 membranes with MWCO being close to 450 Da were pre-selected for the
155 APALD coating.

156



157

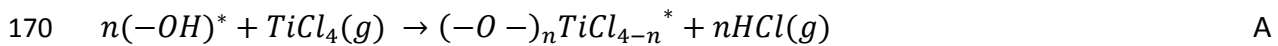
158 Figure 1. Scanning electron microscope (SEM) micrographs of cross-section of the as-
 159 received pristine membrane. 1: separation layer (0.05 μm); 2-5: intermediate layers (0.8 μm;
 160 18 μm; 15 μm; 18 μm); 6: support layer.

161

162 2.2 Atmospheric pressure atomic layer deposition (APALD)

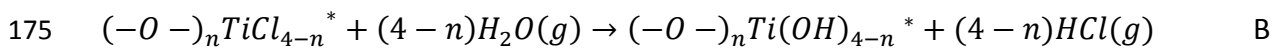
163 A flow-type APALD reactor (Delft IMP B.V., Delft, the Netherlands) was used for coating TiO_2
 164 onto the substrates, including the inner and outer surface of the channel (Figure 2). Titanium

165 tetrachloride, $TiCl_4$ (Sigma-Aldrich/Fluka, the Netherlands) and demineralized water vapour,
166 H_2O , both diluted in a stream of nitrogen gas, N_2 (HiQ 5.0, Linde Gas Benelux, the
167 Netherlands), were used as precursors. In the reactor, the precursors flowed over the
168 substrate in a direction parallel to its surface. When $TiCl_4$ was exposed to the substrate, it
169 chemisorbed and the following reaction (A) took place:



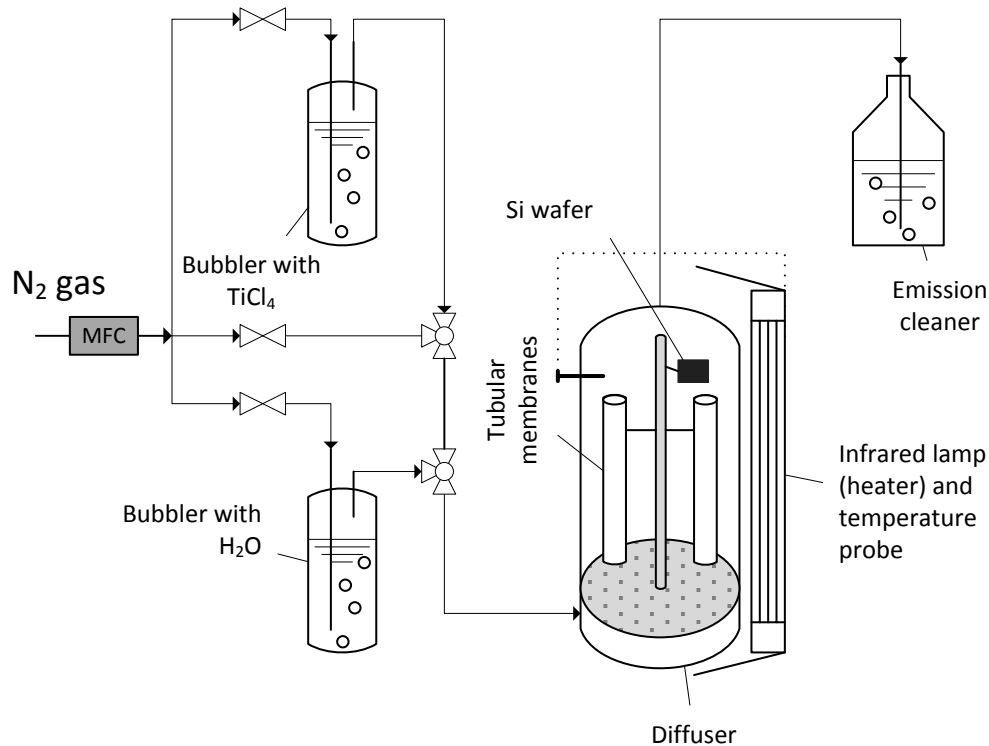
171 where the asterisks denote the surface species.

172 Thereafter, the excessive $TiCl_4$ and generated hydrochloric acid, HCl , vapours were purged
173 using dry N_2 , and then the co-reactant H_2O was introduced to finish one cycle of coating
174 with the following reaction (B):



176 Thereafter, the reactor was purged again to cleanse the residual H_2O and produced HCl
177 vapours. The alternating A-B cycles led to a progressively increasing thickness of TiO_2 on the
178 substrates. In the current study, the APALD reactor was heated to $180^\circ C$ during the process
179 by using an infrared lamp connected to a digital temperature probe. The precursor exposure
180 and purging times were 5 s and 300 s, respectively. The conditions are summarized in Table
181 S1 of the Supplementary Material. A long purging time of 300 s was used in this study to
182 prevent uncontrolled growth of TiO_2 inside the pores because the excessive precursors need
183 to diffuse to the nitrogen purging gas and the diffusion process will take longer than the time
184 needed to purge a non-porous surface [28].

185



186

187

Figure 2. Schematic overview of the APALD setup

188

189 The substrate membranes were fixed vertically in the up-flow reactor (Figure 2). Silicon
 190 witness wafers were placed next to the membranes to monitor the thickness of the coated
 191 layer which was measured by an ellipsometer (M-2000F, J.A.Woollam Co. Inc., USA). By
 192 analysing the change of light polarization, the ellipsometer determines the thickness of thin
 193 layers within a few angstroms of accuracy. However, the substrate membranes used in this
 194 study have a tubular configuration. Direct measurement of coating thickness on the curved
 195 surface of the separation layer was therefore not feasible. Instead, surrogate silicon wafers
 196 of 1 cm x 2 cm with a flat surface were used for monitoring the layer growth by the
 197 ellipsometer.

198 The thickness of the native oxide layer (SiO_2) on the surface of each silicon wafer was
199 measured as a reference using the ellipsometer. After the coating of the wafers, the
200 thickness of the coated TiO_2 layer was again determined using the ellipsometer, deducting
201 the thickness of the premeasured SiO_2 layer.

202 Additionally, the silicon wafers were used to measure the growth-per-cycle (GPC) in the
203 APALD system. The silicon wafers were coated with TiO_2 via 1, 3, 8 and 13 cycles of APALD,
204 using the same coating conditions as used for membrane coating. The obtained linear
205 regression between coating thickness and the coating cycles describes the process GPC.

206 The topography and surface roughness of the silicon wafers were also analysed in order to
207 check the coating quality, using an atomic force microscopy (AFM, Dimension Fast scan
208 Bruker). Again, the analysis was only done on the silicon wafers. The AFM measurements of
209 the pristine and coated silicon wafers were performed ex-situ, right after the deposition. The
210 surface roughness was quantitatively identified by both the root mean square roughness
211 (R_q) and the roughness average (R_a).

212

213 2.3 Membrane characterization and performance

214 2.3.1 Molecular weight cut-off (MWCO)

215 The MWCO is defined as the molecular weight of a tracer molecule that is retained with 90%
216 efficiency by the membrane. Polyethylene glycols (PEGs) of molecular weights ranging from
217 200 Da to 1000 Da were used as the tracer molecules. The PEG molecules are non-charged,
218 and therefore their rejection by membranes is the result of steric rejection. A feed solution,
219 containing a mixture of the PEGs with a concentration of 0.6 g L^{-1} of each, was filtered

220 through the pristine and coated membranes, at room temperature and in cross-flow mode.
221 The feed solution permeated the wall of the tubular ceramic membranes (inside-out) under
222 a constant trans-membrane pressure (TMP) of 4 bar and a cross-flow velocity greater than 1
223 m s⁻¹. The PEG molecules that are smaller than the diameter of the pores in the membrane
224 pass through it; the larger molecules are retained by the membrane and return to the feed
225 solution. Use of mixture of PEGs tends to underestimate the MWCO and pore size of the
226 membrane as the larger solutes will hinder the permeation of smaller ones. The influence of
227 TMP and PEG concentration on the MWCO measurement was evaluated. The results showed
228 that an increased TMP led to a decreased MWCO, while the concentration of PEG, from 0.2
229 to 2 g L⁻¹ for each compound, showed no influence on the measured MWCO (Figure S2 and
230 S3 in the Supplementary Material). In this study, a TMP of 4 bar was selected in order to
231 compare the results with that measured by the manufacturer [7].

232 To calculate the MWCO, both the feed solution and the permeate solution were analysed by
233 a high-performance liquid chromatography system (HPLC, Shimadzu, Japan) equipped with
234 size exclusion chromatography columns (SEC, 5 µm 30 Å, PSS Polymer Standards Service
235 GmbH, Germany). These analyses generated molecular weight distribution curves of the
236 dissolved PEG molecules in the feed and permeate solutions. The corresponding retention
237 curves were then plotted by determining the rejection rate of a PEG with certain molecular
238 weight (R_i) using the following equation:

$$239 \quad R_i(\%) = \left(\frac{C_{i,feed} - C_{i,permeate}}{C_{i,feed}} \right) \quad (1)$$

240 where, $C_{i,feed}$ and $C_{i,permeate}$ are the PEG concentration in the feed and permeate
241 solutions. Afterwards, the experimental rejection curves were described by a log-normal
242 model as a function of MW and $MWCO$, given by Eq. 2 [29, 30]:

243
$$\sigma(MW_s) = \int_0^{MW_s} \frac{1}{S_{MW}\sqrt{2\pi}} \frac{1}{MW} \exp\left[-\frac{(\ln(MW)-\ln(MWCO)+0.56S_{MW})^2}{2S_{MW}^2}\right] dMW \quad (2)$$

244 where $\sigma(MW_s)$ is the reflection coefficient for a PEG with a molecular weight MW_s , S_{MW} is
 245 the standard deviation of the molecular weight distribution.

246 Further, it is assumed that the pore size of the NF membrane follows a log-normal
 247 distribution, and the separation mechanism is based on size exclusion with negligible solute
 248 diffusion. The molecular size of PEG tracers (d_s in nm) is correlated to their molecular weight
 249 (MW in Da) [30]:

250
$$d_s = 0.065(MW)^{0.438} \quad (3)$$

251

252 2.3.2 Permeability of the membranes

253 Water filtration performance was examined by the temperature-corrected permeability.
 254 Demineralized water was filtered at a constant TMP of 4 bar. Membrane fluxes and water
 255 temperature were monitored. An increase of water temperature, from 17 to 25 °C, was
 256 observed during the water filtration experiments due to heat conduction from the cross-flow
 257 pump. The temperature-corrected permeability at 20 °C was calculated using the following
 258 equation:

259
$$L_{p,20^\circ\text{C}} = \frac{J}{\Delta P} \cdot \frac{\eta_T}{\eta_{20}} = \frac{J \cdot e^{-0.0239 \cdot (T-20)}}{\Delta P} \quad (4)$$

260 where $L_{p,20^\circ\text{C}}$ is the permeability at 20 °C ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$), J is the measured membrane flux
 261 ($\text{L m}^{-2} \text{h}^{-1}$), ΔP is the measured TMP (bar), T is temperature of water (°C), and η_{20} and η_T are
 262 the permeate viscosity at 20 °C and at the measured water temperature.

263 2.3.3 Active pore size and BET pore size determination

264 The active pores, which determine the steric rejection of the membrane, are defined as the
265 pores with full coverage over the membrane surface [31]. The active pore size distribution
266 was derived from the PEG rejection profile using the log-normal model as described in
267 section 2.3.1.

268 Physical adsorption of gas molecules on a surface as described by the Brunauer-Emmett-
269 Teller (BET) theory offers another tool to measure pore size distribution in the ceramic
270 membranes. However, the BET method detects pores of various pore sizes, including more
271 than the active pores [32]. Therefore, the pore size distribution of the pristine membranes
272 and the coated membranes were also characterized using the CO₂ adsorption method
273 according to the BET theory. The adsorption/desorption isotherms with CO₂ as adsorbate
274 were recorded at 298 K using a pore size analyser (Autosorb 6B, Quantachrome Instruments,
275 USA). Prior to the adsorption measurements, the tubular membranes were crushed using a
276 mortar and pestle, and degassed in a vacuum for 16 h at 120 °C. The dry samples weight
277 obtained after the pre-treatment was taken into account in the calculations.

278 In BET measurements, the physical adsorption of nitrogen (N₂) gas molecules at a
279 temperature of 77 K is typically used instead of CO₂ adsorption. However, the drawback of
280 using N₂ as an adsorbate for measuring micropores is the very slow diffusion rate into the
281 micropores at a relatively low temperature (77 K) [33]. Therefore, CO₂ adsorption at 298 K
282 was preferred due to the faster kinetics under the higher operational temperature. Another
283 advantage of using CO₂ as an adsorbate is that the pore volume can be accurately
284 differentiated in the pore size range between 0.3 to 1.5 nm.

285

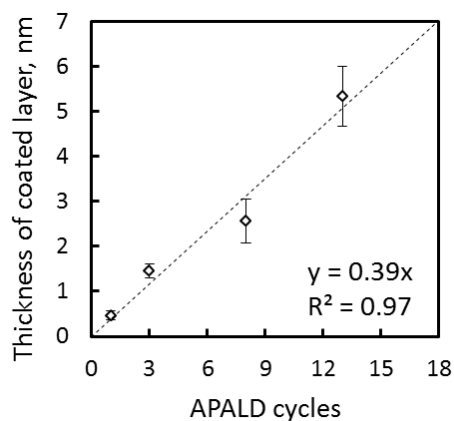
286 **3. Results and discussions**

287 3.1 Thickness and growth kinetics of TiO₂ layers on silicon wafers by APALD

288 The estimated thickness of deposited TiO₂ films on the silicon wafers grows linearly with the
289 increment of coating cycles by the APALD (Figure 3). The GPC is determined to be 0.39 nm
290 per cycle, as obtained from the slope of the linear regression. A growth rate of a few
291 angstrom is typical for ALD under atmospheric pressure on a planar surface, for instance on
292 the surface of particles [25, 34]. In comparison, for ALD of TiO₂ under vacuum conditions, a
293 lower GPC of 0.04-0.06 nm is reported [35-39], because vacuum prevents the formation of
294 precursor and co-reactant multilayers on the substrate surface [25]. In addition, it is more
295 difficult to purge the excess precursors and reaction by-products under atmospheric
296 pressure, albeit the adoption of longer purging times.

297 Despite the relatively high GPC, conforming TiO₂ layers were deposited using the APALD
298 technique, as evidenced by the AFM analysis of the silicon wafers (Figure S4 in the
299 Supplementary Material). The surface roughness of the pristine and coated silicon wafers
300 was between 0.16 and 0.21 nm in terms of root mean square roughness, respectively, and
301 was 0.13 - 0.17 nm in terms of mean roughness. The variation in the measured surface
302 roughness was negligible (always less than 0.05 nm).

303



304

305 Figure 3. Correlation between the thickness of coated TiO₂ layer and the number of APALD
306 cycles for deposition onto silicon wafers. Error bars indicate a standard deviation of 5
307 measurements.

308

309 3.2 Effect of APALD coating on the membrane active pore size and MWCO

310 The coated membranes showed a considerably higher rejection of PEGs of MW 200-400 Da.
311 Based on the PEG rejection and the log-normal model, the size distributions of the active
312 pores in the pristine membranes and the coated membranes of samples 1, 3 and 5 are
313 depicted in Figure 5. The results of the duplicates, sample numbers 2, 4 and 6, can be found
314 in Figure S5 of the Supplementary Material. The average size of the active pores of the
315 coated membranes narrowed from 0.7 nm to 0.5 nm, after one to three cycles of APALD.
316 Furthermore, the coated membranes have more homogeneously-sized active pores,
317 evidenced by their narrower pore size distribution (Figure 5 b, d and f) and their steeper PEG
318 rejection curves (Figure 5 a, c and e).

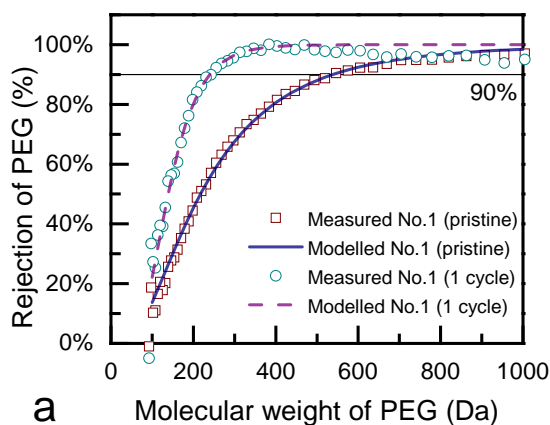
319 Using the CO₂ adsorption method, the pore size distribution in the separation layer of the
320 pristine membranes can be determined. This is because that, in the pristine membranes,
321 only the pores in separation layer fall into the detection range of the applied CO₂ adsorption
322 method (0.3-1.5 nm), since the intermediate layer just underneath the separation layer has a
323 pore size of 5 nm [7]. The majority of pores (90%) were found to be ranging from 0.5 nm to
324 0.8 nm in the separation layer of the pristine membranes (Figure 6). The measured
325 micropore size distribution in the pristine membranes was consistent with the active pore
326 size distribution derived from the PEG/HPLC-measurements (Figure 5). The pores are
327 expected to be symmetrical over the separation layer, since the separation layer is made

328 after a single dip-coating of the polymeric sol [7]. In the APALD-coated membranes, the pore
329 size also ranged from 0.5 nm to 0.8 nm, thus showing a similar result as the pristine
330 membranes. When compared to the pristine membranes, the volume of 0.5-0.6 nm pores
331 slightly increased in the coated membranes, while the volume of 0.6-1.4 nm pores was
332 reduced.

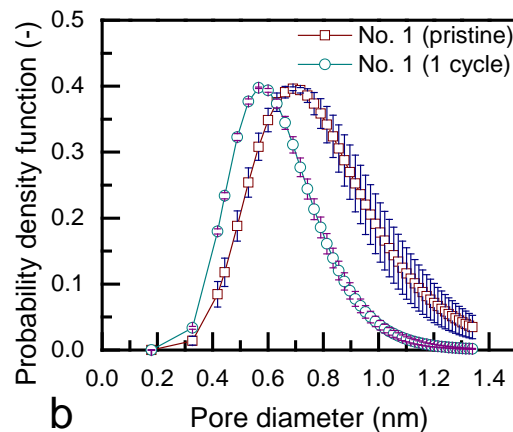
333 The pore size analysis suggested that the growth rate of TiO_2 in micropores was lower than
334 the growth rate on the planar surface of silicon wafer. The metal-source precursor TiCl_4
335 molecule of 0.64 nm [40] tended to preferentially chemisorb in the relatively large pores of
336 0.7-0.8 nm in the separation layer. Since the size of the precursor is comparable to the size
337 of the pores [41], a maximum of one molecule of TiCl_4 was allowed to enter the pore and to
338 chemisorb on the active sites on the pore wall. Therefore, the deposition on the pore wall
339 was likely to be at a much lower rate than the measured growth rate on the planar surface
340 of silicon wafers (0.39 nm per cycle). After one cycle of A-B reaction, the reduction of pore
341 aperture should equal the size of a TiO_2 molecule, reported as 0.04-0.06 nm [35-39]. The
342 MWCO of the coated membranes decreased to 265 – 308 Da after 1, 2 and 3 cycles of
343 APALD, except for sample No. 3 (380 Da) which is likely due to the high MWCO of the No.3
344 pristine membrane (Figure 7). Results obtained using both MWCO and BET measurements
345 confirmed that there was a clear trend of pore size reduction after the deposition. Based on
346 the BET measurements (Figure 6), we observed that micropores in the pristine membrane
347 ranging from 0.8 to 1.4 nm, counting for about 10% of the total pore volume in the
348 separation layer, disappeared after the APALD. It is a clear evidence that the deposition did
349 take place in the pores. However, it remains a question that which fraction of the deposition
350 (deposition in the pores or deposition on the membrane surface) has predominantly
351 contributed to the observed pore size reduction.

352 Unlike the previously reported results of macroporous membrane coating using vacuum ALD
 353 systems [22, 42, 43], a progressive decrease in MWCO with the increase of the APALD cycles
 354 was not observed (Figure 7): the coated NF membranes showed similar MWCO. This
 355 observation might be attributed to the pore-size restricted diffusion of the precursors. As
 356 the molecular diameter of the reactants (0.64 nm) approaches the pore diameter, the pores
 357 may restrict the diffusion of reactants into the membrane pores [41]. As a result, the pore
 358 apertures may reach a minimum value, and the pore aperture will not significantly decrease
 359 with increased APALD cycles.

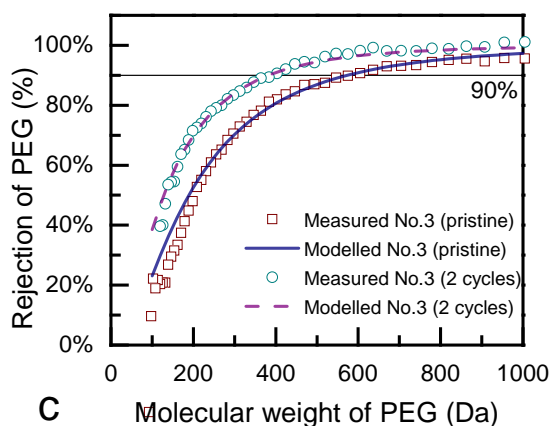
360



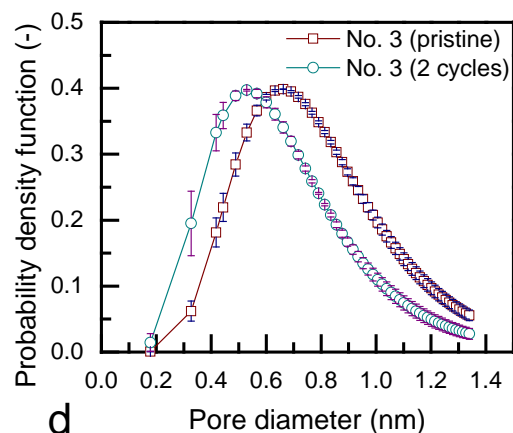
a



b



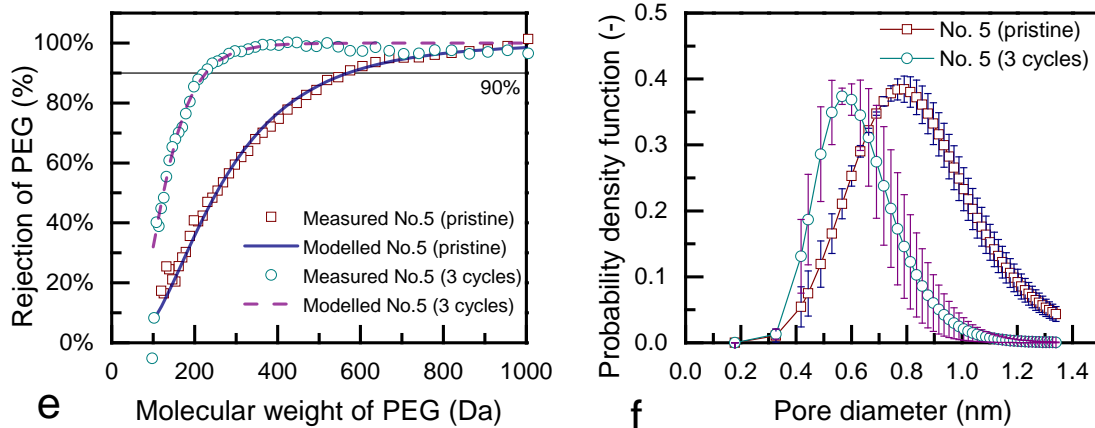
c



d

361

362



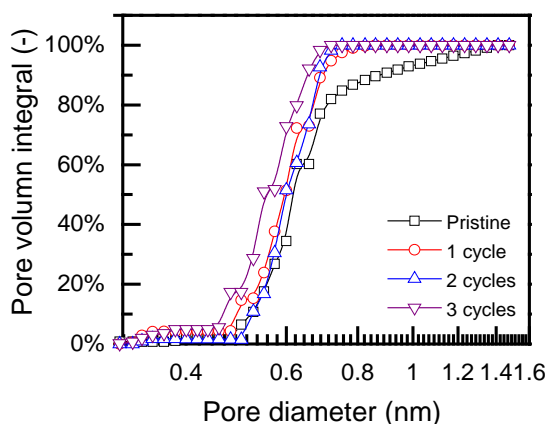
363

364 Figure 5. PEG rejection (a, c and e) and modelled active pore size distribution (b, d and f) of

365 the pristine (substrate) membranes and the coated membranes by APALD (samples No.1,

366 No.3 and No.5). The error bars indicate standard deviation of triplicate samples.

367



368

369 Figure 6. Size distribution of micropores in the pristine and coated membranes (with number

370 of APALD cycles indicated) measured by CO₂ adsorption.

371

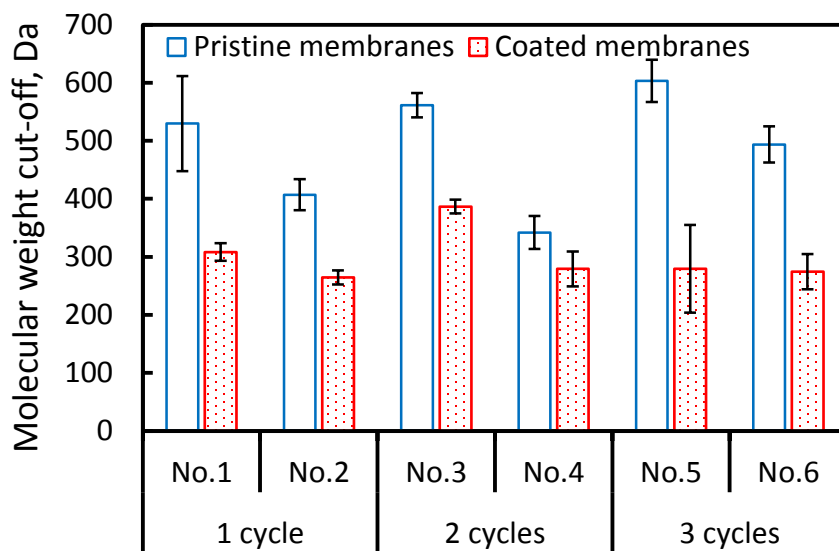
372 In addition, the pore aperture may also be reduced by the growth of TiO₂ on top of the

373 membrane surface at the opening of the pores. The growth on the membrane surface is

374 apparently not influencing the pore sizes. As seen in section 3.1, the growth rate of TiO₂

375 layers on the membrane surface is approximate 0.39 nm per cycle of APALD. This coated
 376 layer build-up on the surface near or at the pore openings may contribute to the reduction
 377 of pore size during the first cycle of ALD. Also, the formed TiO₂ layer was expected to be
 378 porous, having a larger pore size than the size of the active pores. A study by Nikkola, et al.
 379 [44] suggests that the ALD-deposited Al₂O₃ exhibits a loose and porous structure when the
 380 number of applied coating cycles is below 50 (nominal coating thickness of 5 nm), and the
 381 pore size in this structure is larger than the micropores of the coated polymeric RO
 382 membranes.

383



384

385 Figure 7. Molecular weight cut-off (MWCO) of the pristine (substrate) membranes and the
 386 coated membranes using APALD. The error bars indicate the standard deviation of triplicate
 387 measurements. The instinct variation on the MWCO of pristine membrane was substrate-
 388 dependent.

389

390 3.3 Correlation of pore size characteristics to permeability

391 Due to the reduced pore size and porosity in the coated membranes, their permeability
 392 decreased as compared to the pristine membranes (Table 1). The coated membranes of
 393 MWCO ranging from 260 to 380 Da have a permeability between 11 and 16 L m⁻² h⁻¹ bar⁻¹.
 394 It was observed that the water permeability slightly decreased with incremental coating
 395 cycles (Table 1). This may be because of the impregnation and deposition of precursors into
 396 the porous separation layer [22, 23, 42]. A relatively long exposure time (5 s) was applied in
 397 the APALD process. This promotes the diffusion of precursors into the membrane pores,
 398 leading to an increased depth of deposition. A deeper impregnation and deposition of TiO₂
 399 results in a greater loss of porosity in the separation layer, and therefore a lower membrane
 400 permeability. Furthermore, the impregnation can occur from both the membrane surface
 401 and from the support layer via intermediate layers, since the support layer of the substrate
 402 was not sealed during the coating process.

403
 404 Table 1. The MWCO and temperature corrected permeability of the pristine membranes, the
 405 coated membranes (average ± standard deviation from at least 3 measurements).

Type of membrane	MWCO (measured), Da	Permeability at 20 °C, L m ⁻² h ⁻¹ bar ⁻¹
450 Da CNF	490 ± 99	26 ± 7
APALD-coated CNF (1-cycle ALD coated)	287 ± 27	16 ± 5

APALD-coated CNF (2-cycle ALD coated)	333 ± 62	14 ± 0.3
APALD-coated CNF (3-cycle ALD coated)	277 ± 47	11 ± 3

406

407 The growth of the TiO₂ layer on the membrane surface may have had a negligible impact on
 408 the permeability. Nikkola, et al. [44] deposited Al₂O₃ on reverse osmosis (RO) membranes
 409 using 10-100 cycles of ALD. Due to the described effect of pore restriction (section 3.2), the
 410 growth of Al₂O₃ occurred solely on top of the RO membrane surface. They observed that the
 411 membrane permeability had minor changes when the ALD cycle number was below 50
 412 (nominal coating thickness of 5 nm). When the coating cycle increased to 100, a lower
 413 permeability was measured, likely due to compaction of the loosely deposited layers with
 414 incremental deposition cycles. Similarly, the TiO₂ layer on the membrane surface, deposited
 415 with less than or equal to 3 cycles of APALD, should have had a minor influence on the
 416 permeability.

417 The commercial polymeric NF90 and NF270 nanofiltration membranes have similar MWCO,
 418 200-400Da [45], to the coated tight ceramic NF membranes. However, the NF90 and NF270
 419 membranes have water permeability of 7 and 12 L m⁻² h⁻¹ bar⁻¹, respectively [46], which are
 420 slightly lower than the permeability of the APALD-made tight ceramic NF membranes.

421 Furthermore, the APALD-made tight ceramic NF membranes showed significantly higher
 422 permeability than the sol-gel-made counterparts. Van Gestel, et al. [10] synthesized tight
 423 ceramic NF membranes with a ZrO₂ separation layer via the sol-gel method; the resulting
 424 membrane had a MWCO of 300 Da, but its permeability was 2.5 L m⁻² h⁻¹ bar⁻¹. The results

425 demonstrate that APALD is an effective approach for fabricating tight ceramic NF
426 membranes for water treatment. Particularly, water permeability is a crucial economic
427 factor in water treatment practices, influencing both investment and operational costs.
428 Additionally, in the water treatment systems the water permeability is strongly dependent
429 on the composition of the feed water. A significant decrease of water permeability may
430 occur when the tight ceramic NF membranes are used for filtration of real wastewater, due
431 to complex of foulants-membrane interactions (e.g. cake layer formation[17, 47-49], pore
432 blockage [50], pore narrowing due to adsorption [51, 52], calcium-bridged organic
433 fouling[47, 53-55], etc.). Further research on the performance of the tight ceramic NF
434 membranes using real (waste)water is therefore imperative.

435 An optimized, well-controlled exposure/purging sequence is crucial in the APALD procedure
436 for ceramic membranes. Kemell, et al. [28] coated Al_2O_3 to a porous material (pore size
437 approximately 2 μm), and they observed a more conforming coating inside the porous
438 material using longer purge times. Interestingly, Wang, et al. [43] suggested altering the
439 exposure time as an effective way to fine tune the growth rate in the membrane pores.
440 Further knowledge is thus required towards the optimization of exposure/purging sequence
441 times for precursors during the coating of membrane substrates using APALD, although
442 several studies have already been conducted using the conventional ALD systems operated
443 at vacuum conditions.

444

445 **4. Conclusion**

446 In this study, a new route to fabricate tight ceramic NF membranes with high water
447 permeability using atmospheric pressure atomic layer deposition (APALD) is demonstrated.

448 Utilizing APALD enables simpler and more economical processing of the membranes,
449 compared to the conventionally reported ALD schemes that typically require operation
450 under high vacuum conditions. Commercial ceramic NF membranes with an average MWCO
451 of 450 Da were coated with TiO₂. The fabricated ceramic tight NF membranes showed a
452 higher rejection of organic molecules that have molecular weights between 200 and 400 Da,
453 compared to the uncoated membranes. Their MWCO ranges from 260 to 380 Da, dependent
454 on the varied as-received substrate MWCO (400 – 600 Da).

455 The TiO₂ growth per APALD cycle is 0.39 nm on planar surfaces of silicon wafers. However, a
456 maximum one molecule of TiCl₄ precursor is allowed to enter the membrane pores that
457 have comparable sizes to the precursor molecular diameter. As a result, the growth rate on
458 the membrane pore walls is much lower. The average size of active pores was narrowed by
459 approximately 0.2 nm, from 0.7 nm to 0.5 nm, after one to three cycles of coating.

460 Yet, the water permeability remained high, 11 - 16 L m⁻² h⁻¹ bar⁻¹, which is higher than the
461 commercial tight polymeric NF and the sol-gel-made tight ceramic NF membranes that have
462 comparable MWCO.

463

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