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1 **Simple and efficient method for functionalizing photocatalytic ceramic membranes and**
2 **assessment of its applicability for wastewater treatment in up-scalable membrane reactors**

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10 **Abstract**

11 A photocatalytically active layer composed of TiO₂ (Evonik P25) was successfully deposited on
12 the macroporous (3 μm pore size) permeate side of an asymmetric porous alumina membrane with
13 the aid of a smectite (a synthetic hectorite, Sumecton SWF) by dipping the membranes into an
14 aqueous suspension containing P25 and the smectite. After the heat treatment at 400 °C, the coated
15 hybrid was adhered on the macroporous support enough to be applied for the photocatalytic
16 decomposition of organics (methylene blue and phenol as model molecules) in water. The water
17 permeance of the membranes after the coating with the P25-smectite hybrid was reduced by only
18 24% compared with that of the pristine membrane, showing that the advantages of the present
19 method for the preparation of the photocatalyst layer on the surface of the macroporous alumina
20 without significant infiltration of the suspension into the support pores. The amount of MB and
21 phenol degraded using the P25-SWF hybrid was equal to 0.007 and 0.023 mmol.L⁻¹, respectively,

22 when the reaction was carried out using the four single-channel tubular membrane reactor at
23 transmembrane pressures of 250 mbar. The implemented photocatalytic membrane reactor can
24 easily be up-scaled by increase the size of the membrane module, with more tubes and longer tubes
25 (lengths up to 1 m are commercially available), paving the way to potential technological
26 applications for the continuous treatment of polluted waters.

27 Keywords: photocatalytic membrane; hybrid suspension; titania; smectite; organics
28 photodegradation; wastewater treatment

29

30 **1. Introduction**

31 The deposition of semiconductor photocatalysts on solid supports has been extensively
32 investigated to solve environmental problems (air and water contamination) by the photocatalytic
33 decomposition of organic compounds in gas phase thanks to the unique characteristics of
34 photocatalytic activity and superhydrophilicity induced by UV light irradiation [1-3] and that in
35 aqueous solutions [4, 5]. Various wet (e.g. dip and spin coating from slurry and suspension) and
36 dry processes (e.g. chemical vapor deposition and sputtering) have been employed to deposit
37 semiconductor photocatalysts on supports [6-11]. Homogeneous coating of semiconductor
38 photocatalysts has been obtained on flat and smooth surface of supports [12-14].

39 Photocatalytic membrane reactor is a hybrid process coupling the separation by membrane
40 and the degradation by heterogeneous photocatalysis supported on the membrane. Ceramic
41 membranes are advantageously used compared with organic polymer membranes considering the
42 degradation of the polymers under UV exposure [15, 16]. Ceramic separation membranes usually
43 possess asymmetric structures with thin separative layer and macroporous support providing the

44 required mechanical resistance. Depending on the membrane type, one or several intermediate
45 layers are required between the separative layer and the macroporous support.

46 Semiconductor photocatalysts have been deposited as the separative layer or on the
47 separative layer of alumina membranes with the average pore size in the range from 0.2 to 0.005
48 μm , corresponding to microfiltration or ultrafiltration membranes [17-20]. Both photocatalyst
49 depositions on the macroporous support and the separative layer have also been reported [21-23].
50 Those membranes were used in applications of fouling prevention [24, 25]. TiO_2 was selected as
51 a semiconductor photocatalyst due to potential to be used to construct photocatalytic membranes
52 in water treatments [26-31]. Another option of photocatalytic membrane is to deposit
53 photocatalysts on a macroporous support in contact with the permeate side, which is illuminated
54 by UV light. An additional advantage of this configuration is to post-functionalize an existing
55 membrane as photocatalyst contactor, without modifying its separative layer, and consequently its
56 retention performance. Few studies have focused on the deposition of TiO_2 on macroporous
57 alumina membrane supports (average pore size $>3 \mu\text{m}$) [32-34] because the deposition of
58 photocatalytic layer homogeneously is difficult and infiltration of the photocatalysts inside the
59 macropores occurs. These may cause an important loss of permeability.

60 Here, a new method is proposed to deposit semiconductor photocatalysts on porous
61 supports, which is based on the simple addition of smectites in the suspension of TiO_2 particles
62 and subsequent drying of the suspension on the porous support. Smectite (a group of clay minerals)
63 is used as the additive in the present study, which acts as a rheology controlling agent to disperse
64 TiO_2 in water and also acts as a binder upon solvent evaporation. Smectite has been used as an
65 additive in paints due to its swelling properties by the expansion of the interlayer space in solvents
66 (water and organic) [35]. The hybridization of TiO_2 with smectite for photocatalysts application

67 has been reported to modify the reactions and processes [36, 37]. Among available smectites, a
68 synthetic hectorite (Sumecton SWF) was used because it is relatively pure for both phase and
69 element (chemical formula; $\text{Na}_{0.3}(\text{Mg},\text{Li})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) compared with natural smectites. The
70 purity and finite particle size (less than 100 nm) of hectorite are important for the present study in
71 order to minimize light scattering resulted from the particles and no un-wanted absorption of light
72 by the impurities. Herein, the hectorite (Sumecton SWF) was chosen as the additive by taking
73 advantages of the rheological and structural characteristics in order to deposit semiconductor
74 photocatalysts (TiO_2 particles) on macroporous support for the construction of photocatalytic
75 membranes.

76 The deposition of the photocatalyst layer was done by dipping flat or tubular macroporous
77 alumina membranes into the aqueous suspension containing TiO_2 and the hectorite. The permeate
78 flow measurements were performed for measuring the water permeability change of the
79 membranes after their functionalization. The TiO_2 -hectorite hybrid coated on the alumina support
80 was applied as the photocatalytic membrane to assess the decomposition of organics (e.g. dye and
81 phenol) in contaminated water.

82 **2. Experimental**

83 **2.1. Materials**

84 TiO_2 (Evonik P25) with the average primary particle size of 21 nm and the specific surface
85 area (BET) of $50 \pm 15 \text{ m}^2/\text{g}$ was purchased from Aerosil Co., Ltd. A synthetic hectorite (Sumecton
86 SWF) was kindly donated from Kunimine Industrial Co., Ltd. The cation exchange capacity of the
87 hectorite is 70 mequiv/100 g of clay. Methylene blue and phenol were purchased from Aldrich
88 Co., Ltd. All the chemicals were used without further purification.

89 The used alumina microfiltration membranes were supplied by Fraunhofer Institute for
90 Ceramic Technologies and Systems (IKTS), Germany. They exhibited an asymmetric structure
91 consisting of the macroporous support with the average pore size of 3 μm , the intermediate layer
92 with the average pore size of 0.8 μm and the separative layer with the average pore size of 0.2 μm .
93 Two types of membranes were used; (1) alumina disk with the diameter of 4.7 cm and the overall
94 thickness of 1 mm and (2) alumina tube with the length of 20 cm, inner diameter of 0.7 cm and
95 outer diameter of 1 cm, the separative layer being local in the internal side of the tube. Here,
96 microfiltration membranes were selected because of their higher permeability compared with that
97 of ultrafiltration or nanofiltration membranes with the same macroporous support while
98 accompanying more intermediate layers and a mesoporous or microporous separative layer. Thus,
99 the expected change of the water permeance before and after the coating is more important for
100 microfiltration membranes.

101 **2.2.Preparation and characterization of photocatalytic membrane**

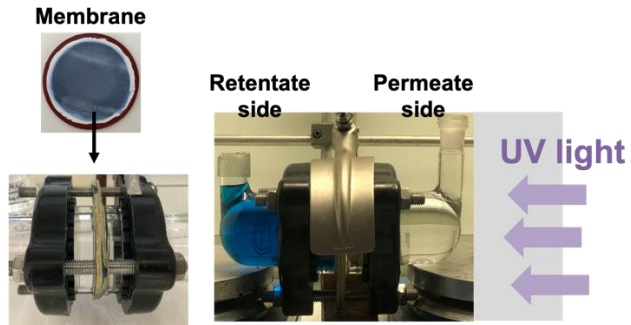
102 The photocatalytic membranes were prepared by dipping the alumina support into the
103 aqueous suspension containing P25 and the hectorite (SWF) at 1 to 10 of SWF to P25 mass ratio
104 with fixing the withdrawal rate of 1 $\text{cm}\cdot\text{min}^{-1}$. In the case of the flat membrane, the side
105 corresponding to the separative layer was temporary protected by a sticky film for avoiding any
106 deposition or infiltration from that side during the dip-coating stage. For the tubular membranes,
107 the tube ends were temporary closed for the same reason. After deposition, the functionalized
108 membranes were dried at room temperature for one day and then thermally treated up to 400°C
109 for one hour for mechanically stabilizing the deposit. Scanning electron microscope (SEM, S-4800
110 Hitachi) was used to observe the morphology of the deposited layer of hybrid on the alumina
111 support. For some structural characterization, analogous powder sample was prepared by pouring

112 a hybrid suspension with the volume fraction of P25 in the suspension of 0.35 % in a beaker.
113 Resulting powder after drying and heating at 400 °C was characterized by nitrogen adsorption-
114 desorption at 77 K using an ASAP 2020 apparatus (Micromeritics). The sample was degassed at
115 250 °C under vacuum before the adsorption-desorption measurements. The mesopore size
116 distribution was determined by the BJH method from the absorption isotherm. The mercury
117 porosimetry (a model of Micromeritics' AutoPore IV 9500 Series) was also used to complete the
118 porosity analysis of the hybrid powder.

119 **2.3.Evaluation of the photocatalytic activity with the membrane reactors**

120 The procedure to evaluate the performance of the photocatalytic membrane was previously
121 developed where the photocatalytic performance was determined as the specific degradation rate,
122 δ , corresponding to the number of mole of compound degraded by unit of membrane area and unit
123 of time ($\text{mol.m}^{-2}\text{s}^{-1}$) [20, 30]. Briefly, the experiment was done by using the diffusion cell reactor
124 (Figure 1), where the feed side was filled with the aqueous MB solution (concentration = 10^{-4} M),
125 while the reception side was filled with pure water. The methylene blue (MB), used as a model
126 molecule, was diffused from the feed side through the membrane (flat membrane coated on the
127 permeate side with P25-SWF) and degraded at the permeate side, where the UV light was
128 irradiated. The measured irradiance from the UV lamp on the functionalized side of the membrane
129 was of 35 W.m^{-2} . The MB concentration in the reception tank was measured by colorimetry at
130 wavelength = 664 nm.

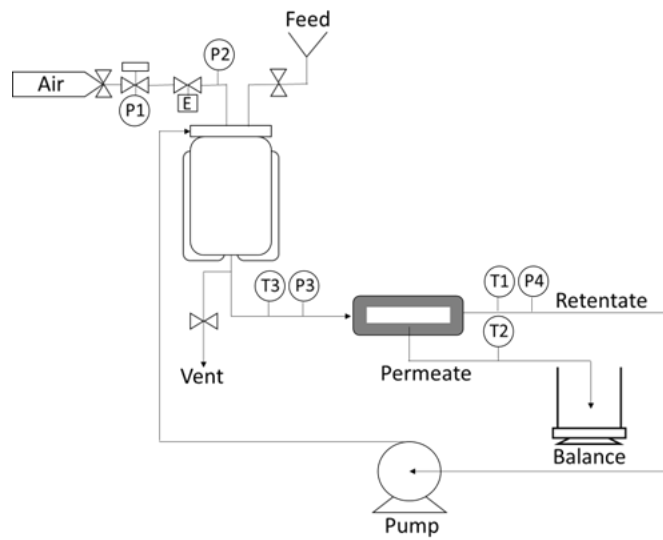
131 The up-scalable membrane reactor (Figure 2) has specifically been developed in the
132 present study for evaluating the reaction efficiency of the tubular membranes in the operation from
133 the expectation to utilize in practical applications for wastewater treatment after up-scaling. The
134 schematic diagram and the photographs of the designed membrane reactor are shown in Figure 2.



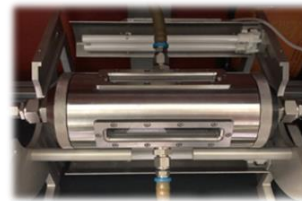
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Figure 1. Diffusion cell used for measuring the degradation rate δ .

(a)

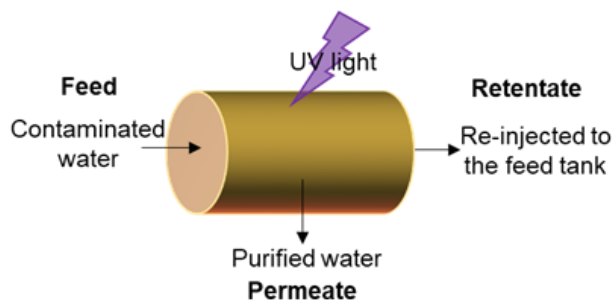


(b1)



(b2)

(c)



136 Figure 2. (a) Up-scalable membrane reactor used for testing the photocatalytic tubular membranes.
137 Schematic representation of the overall pilot. (b1) and (b2) Filtration module equipped with four
138 tubes with an effective length of 15.5 cm (overall filtration area of 136 cm²), four borosilicate
139 windows and four UV lamps. The central part in the module is especially machined for reflecting
140 the light on the tube surfaces not directly accessible by the light beams of the UV lamps. (c)
141 Schematic representation of the tubular membranes with tangential flow of the feed inside the
142 tubes along the separative layer and the UV irradiation on the functionalized permeate side.

143 The maximum volume of solution filled in the feed tank is around 15 liters. The experiment
144 was carried out by applying the transmembrane pressure of 0 – 2 bar using compressed air in the
145 feed tank. The liquid velocity in the membrane loop was 1 m.s⁻¹. The solution at the retentate side
146 was re-injected into the feed tank by the pump, while the solution at the permeate side was
147 collected at the bottom part and weighted. The measured irradiance from the UV lamp on the
148 functionalized side of the membrane was 100 W.m⁻². The MB concentration in the permeate was
149 measured by colorimetry at wavelength = 644 nm using JENWAY 7315 Spectrophotometer. The
150 phenol concentration in the permeated was measured by liquid chromatography with a UV detector
151 (Water 717 Autosample and Water 616 Pump with Water 2996 Photodiode Array Dectector and
152 Thermo Scientific C18 L ¼ 150 mm, I.D. ¼ 4.6 mm column). The change of MB in the permeate
153 without UV irradiation was examined as a control experiment to confirm the decomposition of

154 MB by P25 under the UV light. Gas chromatography coupled with mass spectrometry (GCMS)
155 was used for detecting organic by-products resulting from the partial oxidation of phenol using
156 Thermo Scientific TRACE 1300 and DSQ II with TG-5MS column. The adhesion of the hybrid
157 layer supported on the support after the use for the reaction for two months was examined by SEM.

158 The amount of pure water diffused through the membranes was measured with operating
159 time under different transmembrane pressures, ΔP . The plot of permeate flux J (defined by the
160 volume of pure water at permeate side per unit time and unit of membrane area) versus applied
161 transmembrane pressure (ΔP) for the heated pristine membrane was then drawn. The experiments
162 were done in a cycle loop by increasing transmembrane pressure up to 2 bars, and subsequent
163 decreasing it. The linear trendline was observed after the first cycle with the cyclic increasing and
164 decreasing transmembrane pressure, which is referred to the reliability of the present reactor and
165 operating system. This linear variation of the permeate flux with the transmembrane pressure is in
166 agreement with the Darcy's law;

167 Equation (1) :
$$J = \frac{D}{\eta} \cdot \frac{\Delta P}{L} = Pe \cdot \Delta P$$

168 where J is permeate flux, η is dynamic viscosity of water, D is the intrinsic permeability of the
169 porous membrane, L is the membrane thickness, ΔP is transmembrane pressure, and Pe is the water
170 permeance.

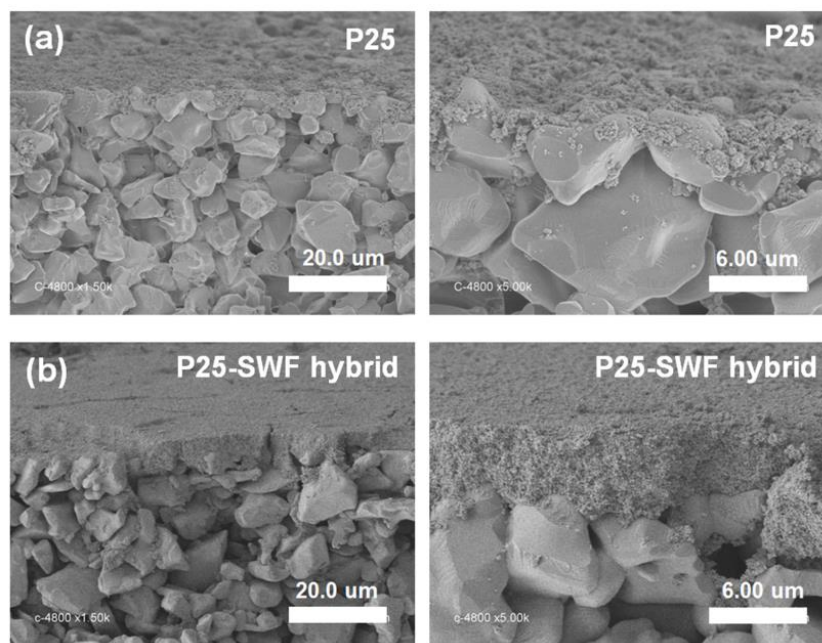
171 The amount of MB degraded can be estimated from the specific degradation rate of MB
172 determined in the diffusion cell reactor and the permeate flux at an applied transmembrane as
173 following equation;

174 Equation (2) :
$$MB \text{ degraded} = \frac{\delta}{\text{Permeate flux}}$$

175 3. Results and discussion

176 **3.1.Functionalization of the alumina membranes**

177 TiO₂ (P25, Evonik) was used as the photocatalyst for the construction of photocatalytic
178 membrane due to its high efficiency for the photocatalytic decomposition of organics [38]. Without
179 additive, the presence of P25 particles on the top surface of macroporous alumina support was
180 observed after dipping the support into the P25 suspension (Figure 3a). On the other hand, when a
181 smectite (synthetic hectorite; Sumecton SWF, hereafter abbreviated as SWF) was added into the
182 P25 suspension, the homogeneously continuous layer of P25-SWF hybrid film was obtained on
183 the macroporous alumina support (Figure 3b).



184
185 Figure 3. SEM images of (a) the P25 and (b) the P25-SWF hybrid at 1 to 10 of SWF to P25 mass
186 ratio coated on porous alumina supports.

187 When SWF was added into the P25 suspension, the viscosity of the suspension increased
188 because of the swelling of SWF. Thanks to the suspension stability, homogenous films of smectite

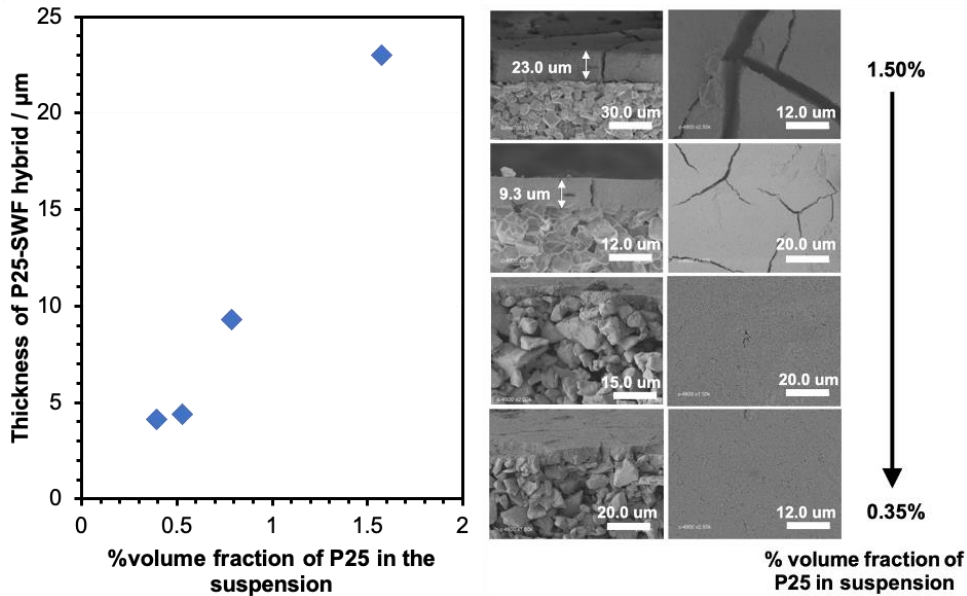
189 with various thicknesses have been prepared by drying the aqueous suspension of smectite on
190 supports [39, 40] as well as by other sophisticated methods including Langmuir-Blodgett [41] and
191 layer-by-layer deposition techniques [42, 43]. It is thought that the probability of the viscous
192 suspension containing P25 and SWF to be infiltrated into the pores of the membrane support was
193 lower than that of the P25 suspension without the addition of SWF, leading the homogeneous
194 coating of the hybrid layer on the macroporous alumina support after the drying.

195 The mass ratio of SWF to P25 was fixed at 1 (SWF) : 10 (P25) based on the previous
196 studies on the hybridization of TiO₂ and smectite film [44, 45], in which the optimum amount of
197 smectite in the hybrid was shown to depend on the particle size of TiO₂. Accordingly, the increase
198 of the SWF content was not examined further to control the viscosity of the suspension in the
199 present study. The volume fraction of P25 in the suspension varied to control the thickness of the
200 coating. The correlation between the thicknesses of P25-SWF hybrid coated on the porous alumina
201 support and the volume fraction of P25 in the suspension is shown in Figure 4. The thickness of
202 P25-SWF hybrid increased from 4 μm to 23 μm with increasing the volume fraction of P25 in the
203 suspension from 0.35 to 1.5 %. However, cracking at the surface was found for the coating from
204 0.75 % and 1.5 % of the volume fraction of P25 in the suspension giving rise to the thicker layers.
205 This phenomenon is due to the development of mechanical stresses across thick porous layers
206 during their drying [46].

207 The volume fraction of solids in the suspension (more than 40%) is required to achieve
208 high viscosity based on the theoretical prediction from a viscosity-concentration behavior [47].
209 Thanks to the smectite, the smaller amount of TiO₂ (0.35% of volume fraction of P25 in the
210 suspension) was enough to obtain the TiO₂ precursor for coating. The present methodology
211 provides an option to control viscosity of the suspension for coating the continuous layer of

212 semiconductor nanoparticles on the macroporous support thanks to the rheological characteristics
213 (swelling properties in water) of smectites. In addition, the eco-friendly materials/method (non-
214 toxic of smectite and no organic solvents for the preparation), as well as the
215 thermal/chemical/mechanical resistances from the robustness of the inorganic-inorganic hybrids,
216 are beneficial aspects for practical uses.

217 Based on the homogeneity with very limited cracking at the coating surface, the hybrid
218 layer with thickness of 4 μm on the macroporous alumina, prepared at the volume fraction of P25
219 in the suspension of 0.35 %, was selected to examine the further experiment for evaluation of the
220 photocatalytic efficiency in the membrane reactors. The equivalent powder was used for
221 characterizing the pore size of this hybrid material. Broad pore size distribution in the range of few
222 nm to a hundred nm with the maximum pore diameter of 70 nm was shown by the nitrogen
223 adsorption-desorption isotherms. (The isotherms are shown in Figure S2.) The existence of such
224 mesopores with the range of size distribution as well as the absence of the additional pores with
225 larger size was confirmed by mercury porosimetry (Figure S3). The selection of microfiltration
226 membranes was made to better estimate the change of permeability after coating. However, in
227 order to avoid any damageable internal fouling of the membrane in operation, ultrafiltration and
228 nanofiltration membranes (with an average pore size less than that of the photocatalytic layer, i.e.
229 70 nm) should be preferred. Such membranes exhibit much lower permeability thus limiting the
230 contribution of the added active layer to the overall drop pressure across the membrane. Moreover,
231 the developed method should easily be adapted for microfiltration membranes by adding pore-
232 forming agents in the hybrid suspension in order to generate larger and interconnected pores in the
233 deposited photocatalytic coating.



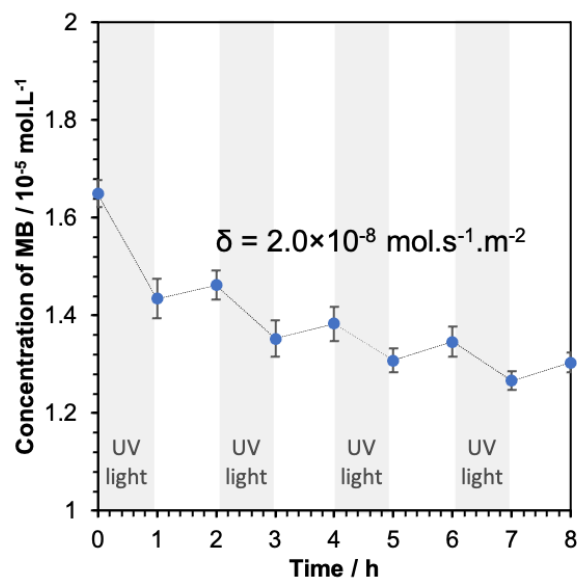
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235 Figure 4. Correlation between the thicknesses of P25-SWF hybrid coated on the alumina versus
 236 % volume fraction of P25 in the suspension and the associated SEM images.

237 3.2 Assessment of the photocatalytic efficiency of the functionalized membranes

238 The efficiency of the layer of P25-SWF hybrid with thickness of 4 μm on a flat membrane
 239 was examined using the diffusion cell reactor, cyclic irradiation periods and by measuring the
 240 evolution of the MB concentration in the reception tank (Figure 5). The procedure to evaluate the
 241 efficiency of photocatalytic membrane was developed by conducting the degradation reaction of
 242 organic dissolved in water (methylene blue, MB commonly used as a model organic molecule) in
 243 the diffusion cell with two compartments separated by the membrane [20, 30]. The amount of a
 244 model organic (MB) degraded per unit area of photoactive surface and per unit time is defined as
 245 the specific degradation rate (δ). The evaluated specific degradation rate, δ , can be used in order
 246 to estimate the size and working conditions for further development on implementation of
 247 photocatalytic membranes in an up-scalable membrane reactor for practical application in
 248 wastewater purification.

249 The UV light was irradiated at the permeate side, where the layered hybrid of P25-SWF
250 was coated on the alumina support. The specific degradation rate (δ) of MB using the P25-SWF
251 hybrid was calculated to $2 \times 10^{-8} \text{ mol.s}^{-1}.\text{m}^{-2}$. Despite the presence of photocatalytically inactive
252 component (SWF), this value is comparable with the specific degradation rate of MB that was
253 previously reported for other photocatalytic membranes (Table S1) [26, 48-50]. A decreased
254 efficiency of the photocatalytic decomposition of stearic acid was observed when the SiO_2 was
255 used as the binder to deposit TiO_2 on the support [51]. The pH of MB solution after the reaction
256 was around 5, which indicated that the adsorption of MB on P25 and the alumina was not plausible
257 because the surface of P25 and alumina are positively charged under the examined conditions. The
258 decomposition of MB could be affected by the adsorption of MB on the smectite (SWF) because
259 the enhanced decomposition of MB by the hybridization of smectite with TiO_2 as the hybrid film
260 was previously reported [44], where the observed efficient decomposition was explained by the
261 attractions between MB and P25.



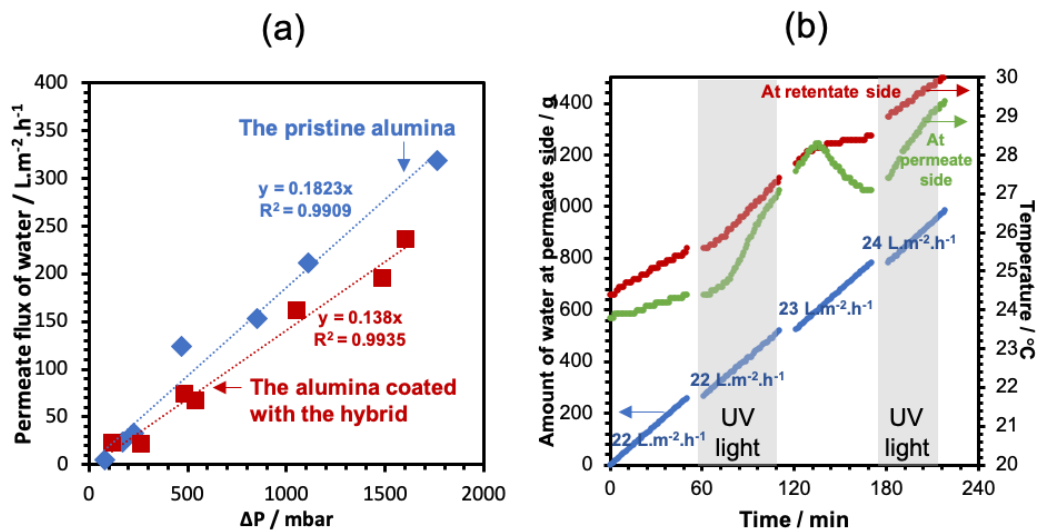
262
263 Figure 5. Photocatalytic decomposition of MB using the membrane of P25-SWF hybrid in the
264 diffusion cell reactor.

265 **3.3 Implementation of the up-scalable photocatalytic membrane reactor with four single-**
266 **channel tubular membranes for wastewater purification**

267 The suspension containing P25-SWF hybrid at 1 to 10 of SWF to P25 mass ratio was used
268 to be coated on the permeate side of four tubular membranes. These membranes were placed in
269 the membrane reactor in order to examine the decomposition of MB and phenol. The liquid
270 velocity inside the loops being fixed at $1 \text{ m}\cdot\text{s}^{-1}$, a turbulent flow was expected in the tubes from the
271 estimation of Reynolds number (ca. 8000). The heat treatment of the pristine membranes under
272 the identical conditions for the membranes coated with the hybrid was done to remove
273 contaminants before measuring the permeate flux. The measured permeate flux of water for the
274 membranes coated with the P25-SWF hybrid decreased if compared with that before the coating
275 as shown in Figure 6a (red square). The water permeances were 182 and $138 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ for the
276 membranes before and after the coating with the hybrid, respectively, as determined from the slope
277 of the linear correlation. The intrinsic membrane permeability D for the membranes before and
278 after the coating with the hybrid was determined to 1.52×10^{-15} and $1.16\times 10^{-15} \text{ m}^2$, respectively,
279 using the Darcy's equation (equation 1).

280 The viscosity of the water flowed inside the tubular membrane is one of the parameters to
281 affect the permeate flux. Viscosity of water strongly depends on temperature. The temperature of
282 water at the permeate and retentate sides was measured during the operation, before and after UV
283 irradiation in order to observe the change of permeate flux along the operation time (Figure 6b).
284 The temperature of pure water at the retentate side (water flowing inside the tubular membrane)
285 changed from 25 to 30°C with longer operation time until 240 min. However, the permeate flux
286 (slope of amount of water at permeate side versus time) was slightly changed from 22 to $24 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$.
287 So, the change of the permeate flux in longer operation time was not concerned.

288 Table 1 shows the reported water permeance using various TiO₂ based membranes. The
 289 significant decrease of the water permeance after the coating of TiO₂ on the separative layer (pore
 290 size < 0.2 μm) of the alumina membranes was observed [49, 52-55]. Permeability of membrane
 291 depends on the porosity of membrane. A significant loss of the permeability (40-80%) was
 292 previously observed, which was explained by the reduction of the porosity from plugging of TiO₂
 293 into the pore of the alumina membranes. In contrast, a lower loss of water permeance (24%) was
 294 here observed for the hybrid coated on the macroporous alumina membrane. This indicates the
 295 advantage of the present method to coat TiO₂-based layer on the macroporous alumina support
 296 without important penalizing effects in terms of permeate flow decrease by minimizing the change
 297 of membrane porosity from the infiltration of the TiO₂ suspension into the pore of alumina. In
 298 addition, the role of the separative layer acting as the separation unit was not disturbed. Such a
 299 limited change of the permeability after the coating is beneficial in terms of process operation to
 300 reach the targeted permeate flux at low transmembrane pressure.



301
 302 Figure 6. (a) Permeate flux of water for the membrane before and after coating with the P25-SWF
 303 hybrid under varied transmembrane pressures and (b) measured amount and temperature of water

304 after on and off cycle of UV irradiation for 1 h with fixing the transmembrane pressure at 125
 305 mbar.

306 Table 1. Comparison of measured water permeance using different TiO₂ membranes.

Sample	Water permeance / L.m ⁻² .h ⁻¹ .bar ⁻¹		Loss of water permeance (%)	Ref.
	Before coating	After coating		
TiO ₂ film on alumina membrane (pore size = 0.2 μm) from commercial hydrosol S5-300B	1800	150	92	[49]
N doped TiO ₂ film on alumina membrane (pore size = 0.2 μm)	3800	1600	58	[52]
TiO ₂ film on alumina membrane (pore size = 0.1 μm)	11	6.71	39	[53]
Si doped TiO ₂ film on alumina membrane (pore size = 0.1 μm)	1950	340	83	[54]
TiO ₂ nanotube inside the alumina template (pore size = 0.2 μm)	40	5	88	[55]
P25-SWF hybrid coated on alumina membrane (pore size = 3 μm)	182	138	24	This work

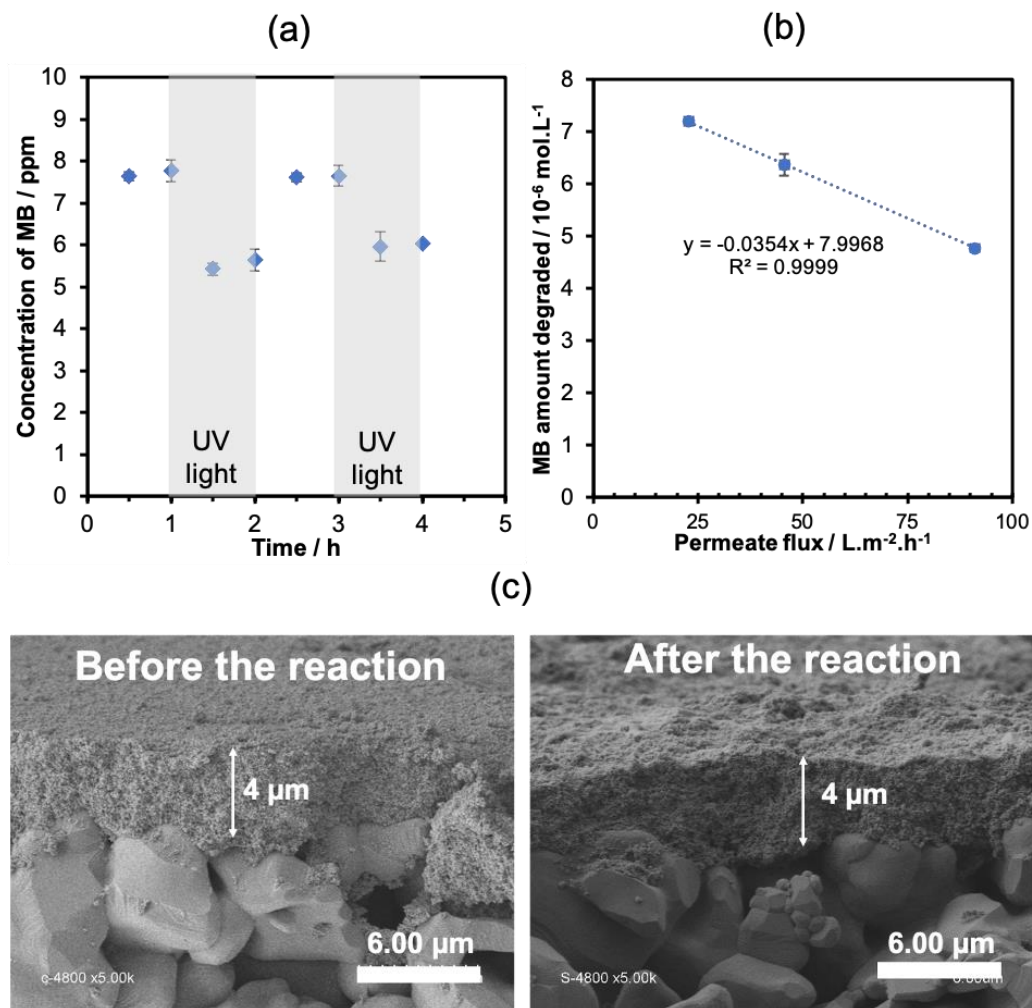
307 Based on the previously estimated specific degradation rate of MB ($\delta = 2 \times 10^{-8} \text{ mol.s}^{-1}.\text{m}^{-2}$)
 308 ²⁾ using the P25-SWF hybrid in the diffusion cell reactor, the degraded amount of MB could be
 309 equal to 0.7 ppm ($2.1 \times 10^{-6} \text{ mol.L}^{-1}$) from the calculation using the equation (2) for an applied
 310 transmembrane of 250 mbar with the permeate flux of $34.5 \text{ L.m}^{-2}.\text{h}^{-1}$ (determined by the slope of
 311 the alumina coated with the hybrid in Figure 6a).

312 As shown in Figure 7a, the decrease of MB concentration at the feed tank from 9 ppm to 8
 313 ppm at permeate before turning on the UV light may be explained by the adsorption of MB
 314 (positively charged dye) on the SWF (negatively charged layer). The decrease of MB
 315 concentration after turning on UV light in a cycle for 1 h from 8 to 6 ppm indicated that the MB
 316 was decomposed by the active species generated on P25 under the UV light irradiation. The
 317 degraded amount of MB after the UV irradiation for 1 h was equal to 2.1 ppm ($6.4 \times 10^{-6} \text{ mol.L}^{-1}$)
 318 when the reaction was conducted at transmembrane pressures of 250 mbar. The amount of MB

319 degraded in the up-scalable membrane reactor is thus higher than the expected amount of MB
320 degraded from the estimation of the result in diffusion cell reactor (2.1×10^{-6} mol.L⁻¹). Efforts to
321 use the similar emission spectra of the UV lamps (315-400 nm) in both diffusion cell and up-
322 scalable membrane reactors have been made in order to minimize the effects of the different
323 absorption of UV light by the P25 from the different wavelength. However, other factors such as
324 irradiance and reaction conditions in both reactors were not identical to unable a direct comparison
325 of the photocatalytic performance.

326 The linear relationship between the amount of MB degraded versus the permeate flux
327 (Figure 7b) indicated that the MB decomposition depends on the probability of contact between
328 MB molecule and active species created at the surface of the P25 nanoparticles. From the permeate
329 flux of 34.5 L.m⁻².h⁻¹ at the applied transmembrane pressure of 250 mbar and the thickness of the
330 photocatalytic layer of 4 μm, the residence time of the MB molecules in this layer was calculated
331 to be only 0.42 second. It must be added that only a few micrometers of the titania-based films, in
332 depth from the UV-irradiated surface, are expected to be photocatalytically active [56]. Finally,
333 the estimated size of the MB molecules (less than 2 nm) is very small in comparison with the pore
334 size of the active layers (70 nm). All these factors can explain that only some part of the MB
335 molecules crossing the membrane were photodegraded.

336 The photocatalytic reaction occurred without any loss the efficiency from leaching of the
337 P25 particles from the alumina support, which referred to the adhesion of the continuous layer of
338 P25-SWF hybrid with the alumina support was strongly enough for the reaction under operating
339 conditions (applying transmembrane pressure). It is confirmed by the presence of similar thickness
340 of layer of hybrid (4 μm) on the macroporous alumina support after use for two months in the
341 membrane reactor, which is seen in the SEM images (Figure 7c).

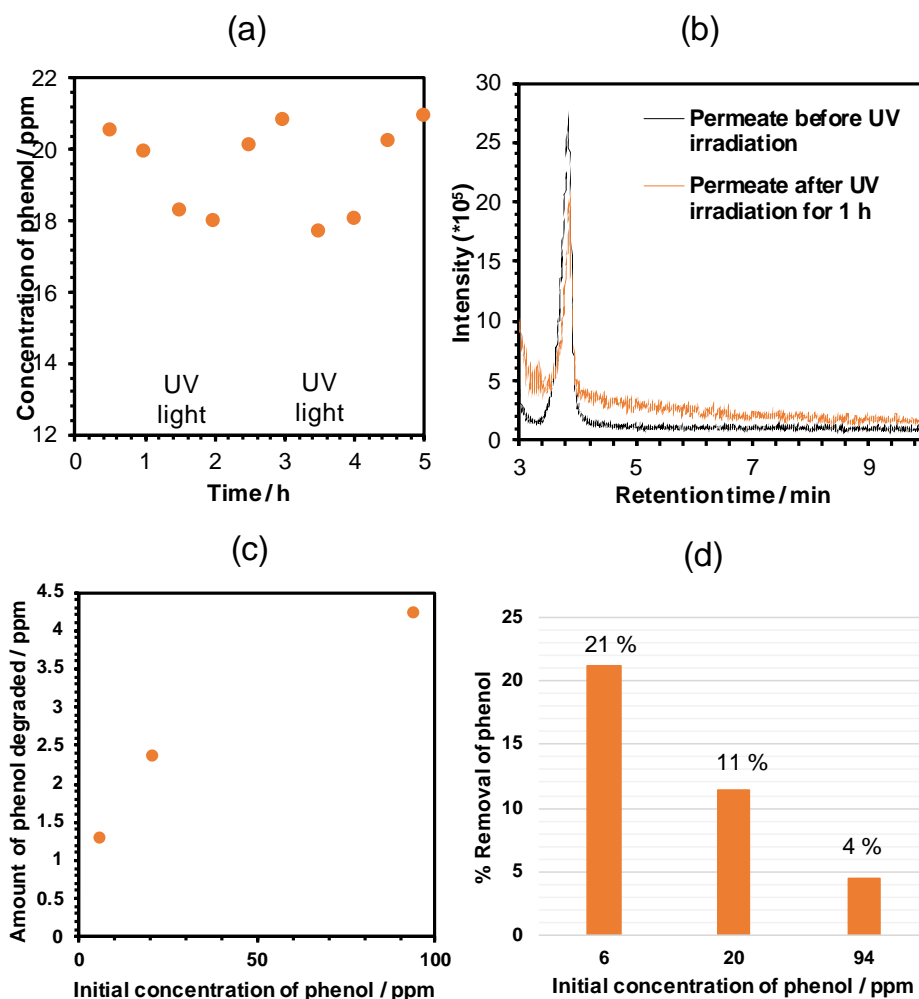


342

343 Figure 7. (a) MB concentration in the permeate with the photocatalytic membrane reactor working
 344 at transmembrane pressure of 250 mbar and cyclic irradiation periods of one hour, (b) relationship
 345 between the amount of MB degraded versus permeate flux and (c) SEM images of the hybrid on
 346 alumina membrane before and after use for two months in the membrane reactor. The initial
 347 concentration of MB in the feed tank is 3×10^{-5} mol.L $^{-1}$ (9 ppm).

348 Phenol was selected as another model organic molecule in contaminated water. The
 349 degraded amount of phenol after UV irradiation for 1 h was equal to 2.4 ppm, when the reaction
 350 was conducted at the transmembrane pressures of 250 mbar (Figure 8a). Based on the previous

351 studies [49], the specific degradation rate using the diffusion reactor for MB and phenol was
352 estimated at the similar value. The estimated value of specific degradation rate of phenol is
353 assumed to be $2.1 \times 10^{-6} \text{ mol.L}^{-1}$ (0.2 ppm), which is very close to the degraded amount of phenol
354 (2.4 ppm) observed at the transmembrane pressures of 250 mbar in the present study. Any organic
355 by-products after the photodegradation of phenol using the P25-SWF hybrid were not detected in
356 the permeate by GC-MS (Figure 8b). Phenol has been detected in groundwater (the range of 1 to
357 10 ppb), in rain (0.075–1.2 ppb), industrial rivers in the United States (5 ppb) [57], and in drinking
358 water (0.5 ppb) according to EU directive [58]. The amount of phenol degraded at varied initial
359 concentration of phenol in the feed was examined (Figure 8c). The experiment at very low
360 concentration of phenol in ppb could not be done at present due to the detection limit (around 100
361 ppb) of the liquid chromatography. However, the mineralization of phenol contaminated in natural
362 water may be possible because the higher percentage of phenol removal at lower initial
363 concentration of phenol was observed (Figure 8d).



364

365 Figure 8. (a) Phenol concentration in the permeate with the photocatalytic membrane reactor
 366 working at transmembrane pressure of 250 mbar and cyclic irradiation periods of one hour. (b)
 367 GC-MS chromatogram of the solution before and after the reaction. The initial concentration of
 368 phenol in the feed tank is $2.2 \times 10^{-4} \text{ mol.L}^{-1}$ (21 ppm). (c) Relationship between the amount of
 369 phenol degraded and the initial concentration of phenol. (d) % Removal of phenol at different
 370 initial concentrations of phenol.

371 Table 2 shows the reported efficiency of the photocatalytic phenol degradation using the
 372 different types of photocatalysts deposited on membranes as supports. If compared with the

373 reported ones, the highest efficiency of phenol degradation is observed in the present study using
374 the P25-SWF hybrid. It can be due to the homogenous deposited film formed with P25 titania
375 nanoparticles known as a very efficient catalyst.

376 Furthermore, the implemented photocatalytic membrane reactor can be easily up-scaled by
377 increase the size of the membrane module, with more tubes and longer tubes (lengths up to 1 m
378 are commercially available), paving the way to potential technological applications for the
379 continuous treatment of polluted waters.

380 **4. Conclusions**

381 The method to deposit a photocatalyst layer on a macroporous material with the aid of a
382 smectite, was developed. By taking advantage of swelling properties of the smectite in water, the
383 deposition of P25 and SWF hybrid was successfully achieved on the macroporous alumina support
384 (3 μm pore size) without significant infiltration by dipping the alumina into the aqueous suspension
385 containing P25 and SWF. The hybrid film (4 μm of thickness) coated on the porous alumina was
386 used as the photocatalytic membrane to examine the decomposition of organics (e.g. dye and
387 phenol) contaminated water using the membrane reactors. The amount of phenol degraded using
388 the P25-SWF hybrid was equal to 0.023 mmol.L^{-1} , when the reaction was carried out using an
389 easily up-scalable photocatalytic membrane reactor with four single-channel tubular membranes
390 at transmembrane pressures of 250 mbar. The present method is applicable for the construction of
391 photocatalytic ultrafiltration and nanofiltration ceramic membranes to be used for water polishing
392 with in an up-scalable continuous flow membrane reactor.

393 Table 2. Photocatalytic degradation of phenol using the different photocatalysts deposited on
394 supports as the photocatalytic membrane.

Sample	Preparation	Permeance (L.m ⁻² .h ⁻¹ .bar ⁻¹)	Amount of phenol decomposed in an hour (mmol.L ⁻¹)	Ref.
TiO ₂ film on alumina membrane from commercial hydrosol S5-300B	Dipping the membrane into the aqueous suspension	150	0.0008	[49]
Carbon nitrile on polyethersulfone membrane	Drying the solution containing carbon nitrile and polymer to produce flat sheet membrane	264	0.006	[59]
TiO ₂ deposited on polypropylene membrane	Immerging polypropylene into the dispersion of TiO ₂	-	0.005	[60]
Carbon nitrile on hydrophilic surface modified polyethersulfone membrane	Drying the solution containing carbon nitrile and polymer to produce flat sheet membrane	22	0.006	[61]
P25-SWF hybrid coated on alumina membrane	Dipping the membrane into the aqueous suspension	138	0.023	This work

395

396 **CRedit authorship contribution statement**

397 **Siwada Deepracha:** Methodology, Formal analysis, Investigation, Writing – Original
398 Draft, Writing – Review & Editing. **Loubna Atfane:** Methodology. **André Ayrat:**
399 Conceptualization, Validation, Formal analysis, Resources, Writing – Review & Editing. **Makoto**
400 **Ogawa:** Conceptualization, Validation, Writing – Review & Editing, Supervision.

401 **Declaration of Completing Interest**

402 The authors declare that they have no known competing financial interests or personal
403 relationships that could have appeared to influence the work reported in this paper.

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412 Petit (IEM) for the LC-UV analyses, and Mr. Guillaume Cazals (Plateforme Balard, LMP) for the
413 GC-MS analyses.

414 **Appendix A. Supplementary data**

415 N₂ adsorption-desorption isotherms and BJH pore size distribution of the equivalent powder of
416 hybrid. The pore size distribution of the equivalent powder of hybrid observed by mercury
417 porosimetry.

418

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