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## Combining chemistry and topography to produce antifouling surfaces, a review

Hippolyte Durand, Amelia Whiteley, Pascal Mailey, Guillaume Nonglaton

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**Combining topography and chemistry to produce  
antibiofouling surfaces – a review**

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Manuscripts

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16 3 *AUTHORS.*  
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20 4 *Hippolyte Durand<sup>‡\*</sup>, Amelia Whiteley<sup>‡</sup>, Pascal Mailley, Guillaume Nonglaton*  
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33 7 Univ. Grenoble Alpes, CEA, LETI, DTBS, F-38000 Grenoble  
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40 9 *KEYWORDS.*  
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45 10 Antibiofouling, antibacterial, topography, surface chemistry, hydrophobic surfaces, hydrophilic  
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48 11 surfaces  
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4 12 ABSTRACT. Despite decades of research on the reduction of surface fouling from biomolecules  
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7 13 or micro-organisms, the ultimate antibiofouling surface remains undiscovered. The recent covid-  
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10 14 19 pandemic strengthened the crucial need for such treatments. Among the numerous approaches  
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13 15 that are able to provide surfaces with antibiofouling properties, chemical, biological and  
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17 16 topographical strategies have been implemented for instance in marine, medical or food industries.  
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19  
20 17 However, many of these methods have a biocidal effect and, with antibioresistance and biocide  
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23 18 resistance a growing threat on humanity, strategies based on reducing adsorption of biomolecules  
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26  
27 19 and micro-organism are necessary for long-term solutions. Bio-inspired strategies, combining both  
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29  
30 20 surface chemistry and topography, are currently at the heart of the best innovative and sustainable  
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33 21 solutions. The synergistic effect of micro/nano-structuration, together with engineered chemical or  
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37 22 biological functionalization is believed to contribute to the development of antibiofouling surfaces.  
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40 23 This review aims to present approaches combining hydrophobic or hydrophilic chemistries with a  
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44 24 specific topography to avoid biofouling in various industrial environments and healthcare facilities.  
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## 48 25 Contents

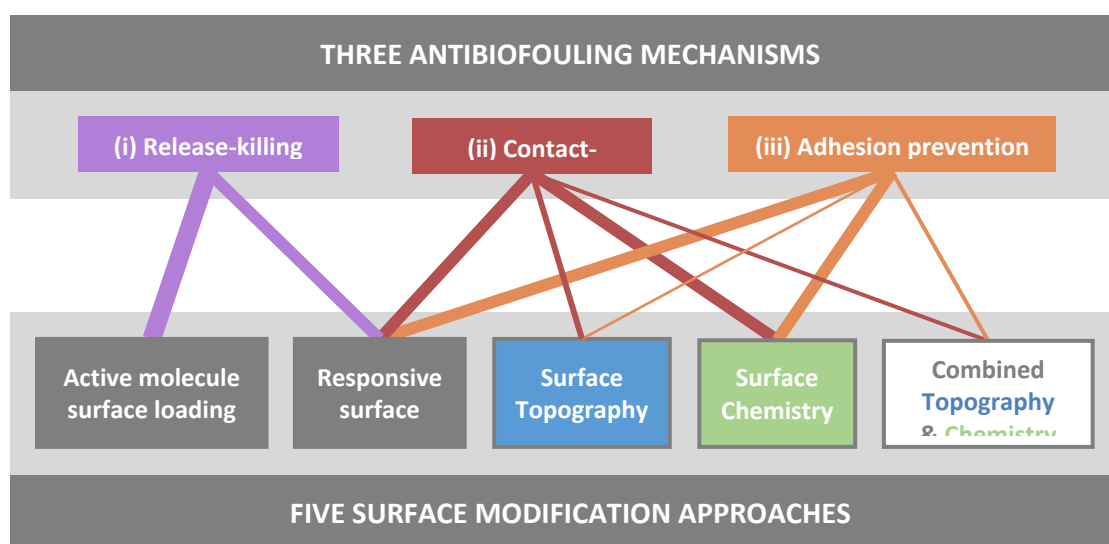
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## 1. Introduction

Surface fouling is defeating man-made devices in various fields. Water treatment<sup>1</sup>, marine<sup>2,3</sup> and food industry<sup>4</sup> as well as the medical field<sup>5-7</sup> are seeking for surfaces that will prevent undesired fouling. This spontaneous deposition of molecules, macromolecules and micro-organisms on an engineered surface upon contact with a liquid medium leads to the formation of biofilms that strongly impede performance and functionality. The predominant use of curative approaches, such as antibiotics in the medical field, or biocides in marine environments, is no longer desirable. Throughout decades of massive administration of antibiotics to human and animal feedstock, more and more resistant bacterial strains have emerged and spread all over the globe. World Health Organization (WHO) recently labelled the arising antibioresistance as the most urgent health threat of our time.<sup>8</sup> And the European Commission forecasts no less than 10 million deaths per year attributed to antibioresistance in 2050 if today's tendency is not hampered.<sup>9</sup> Biocide resistance is also on the rise<sup>10</sup> and the important use of tributyltin since the 1960's has caused tremendous damage to the marine environment.<sup>11,12</sup> Since its prohibition in 2008, more environmentally friendly solutions have been investigated. The scientific community is putting in tremendous efforts in the search for alternative strategies that do not rely only on curative approaches. Their

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4 71 focus is now rather on preventive approaches which tackle the initial steps of biofilm development:  
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7 72 the adsorption of biomolecules and subsequent micro-organisms adhesion. In this manuscript, the  
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10 73 term *antibiofouling* describes the ability of a surface to impede fouling from biological molecules,  
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13 74 macro-molecules and/or micro-organisms, while *antifouling* is used for general fouling with any  
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17 75 type of chemical substance or particle, including inorganic structures. Preventive approaches to  
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20 76 fight surface fouling are now predominantly investigated and can be classified according to three  
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23 77 different mechanisms: (i) active molecule-releasing and (ii) contact-killing surfaces, that prevent  
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27 78 micro-organism growth both on and near surfaces, and (iii) anti-adhesive surfaces that prevent  
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30 79 molecule, macromolecule and micro-organisms adhesion. These three antibiofouling mechanisms  
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34 80 can be achieved with five different types of surface modification, as detailed in Figure 1.



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3 82 *Figure 1: Three antibiofouling mechanisms linked to corresponding types of surface modification. The*  
4 83 *thickness of the links gives an estimation of the amount of research articles on the topics.*

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6 84 (i) In order to fight surface fouling with a limited quantity of antibiotics or biocides, a first  
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10 85 mechanism is active molecule releasing-surfaces. Antibiotic and biocide release will kill the micro-  
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13 86 organisms before they reach the surface and form biofilms. The release can be spontaneous in  
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16 87 *active molecule surface loading* approaches, or triggered by a specific physico-chemical stimuli  
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20 88 (pH, temperature, UV irradiation, enzymatic activity...) in *responsive surface* approaches.  
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23 89 However, these approaches are limited in time, only affect micro-organisms and do not prevent  
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26 90 biomolecular fouling, and still face the issue of antibioresistance, biocide resistance and damage to  
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29  
30 91 the environment. Only short term specific applications will benefit from this mechanism.<sup>3,13,14</sup>  
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34 92 (ii). A second mechanism relies on contact-killing. *Surface chemistry* approaches allow  
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37 93 immobilization of active molecules onto the surface, leading to micro-organisms being killed upon  
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41 94 contact or adhesion. In *responsive surface* approaches, the immobilized active molecule action can  
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44 95 be triggered upon a specific physico-chemical stimuli. Some responsive surfaces are also able to  
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48 96 eliminate the accumulation of dead cells that would progressively impede their contact-killing  
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51 97 effect. But this contact-killing effect can also be obtained without the use of active molecules.  
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54 98 Inspired by numerous natural surfaces in plants and the animal kingdom, engineered surface  
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4 99 topography (nanopillars, microblades, nanospikes...) is able to, in some cases, cause mechanical  
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7 100 stress on adhered micro-organisms, leading to membrane failure and eventually cell death.<sup>15-17</sup>  
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10 101 Hence, *combined surface topography and chemistry* approaches are also able to achieve contact-  
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13 102 killing mechanism, with potential synergistic effects that are reviewed in this manuscript.  
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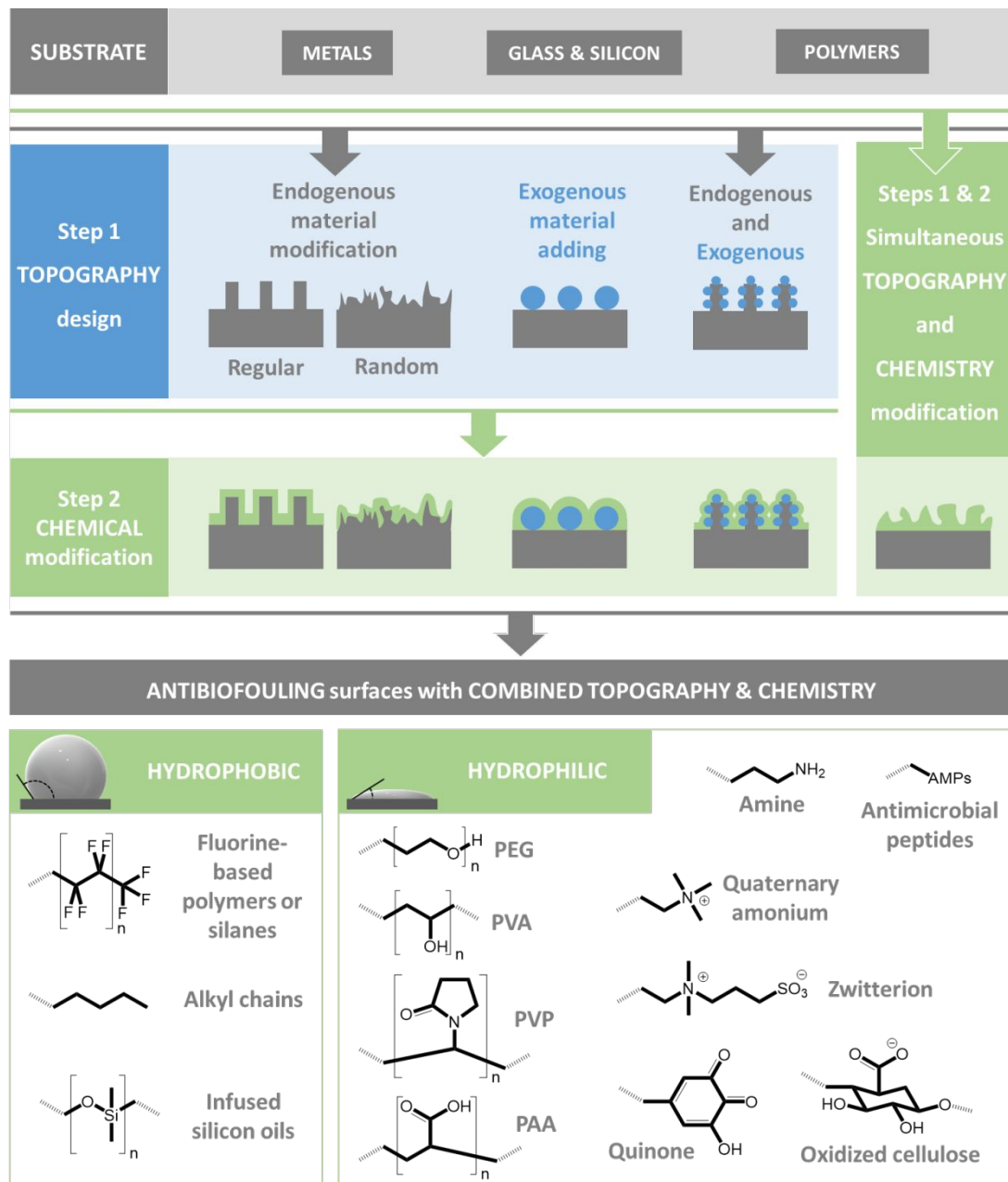
17 103 (iii). At last, only the adhesion prevention mechanism prevents both biomolecules and micro-  
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21 104 organism fouling since they are engineered to prevent the interaction between the foulants and the  
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24 105 surface. For instance, superhydrophobic surfaces obtained by *surface chemistry* or *combined*  
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26  
27 106 *topography and chemistry* approaches will avoid surface fouling since the foulants are confined to  
28  
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30  
31 107 the liquid phase which has a limited contact area with the surface. Similarly, zwitterion molecules  
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34 108 or polymers can provide surfaces with superhydrophilic properties, forming a dense hydration layer  
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37 109 that can also prevent fouling. Plus, depending on physico-chemical stimuli, *responsive surface*  
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41 110 approaches offer similar adhesion prevention mechanisms.<sup>18-20</sup>  
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45 111  
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49 112 All these surface modifications tune the surface properties in terms of topography and/or chemical  
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53 113 composition. Moreover, the still on-going study of natural surfaces in plants, insects and the animal  
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4 114 kingdom have revealed numerous natural antibiofouling strategies that rely on the combination of  
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7 115 a specific surface topography with a particular surface chemistry. The published literature over the  
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10 116 past 5 years offers approximately five hundred reviews on the *antifouling* topic. Within this  
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14 117 overwhelming amount of review articles that cover the afore-mentioned antibiofouling  
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17 118 mechanisms, approximately 60 of them were selected based on their title and abstracts. They were  
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20 119 classified in table S1 of the Supporting information, according to the type of surface modification  
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24 120 approach detailed in Figure 1 (*active molecule surface loading, surface chemistry, surface*  
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26  
27 121 *topography, responsive surface* and *combined topography and chemistry*). Less than ten mention  
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29  
30 122 *combined topography and chemistry* approaches, and never as the core topic of the review.<sup>4,21-27</sup>  
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34 123 Up to our knowledge, none of them specifically focused only on this approach. This manuscript  
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37 124 aims to fill this gap and provide these works with their own specific review. However, these  
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40 125 research articles are not easily identified since authors do not always indicate the combined aspect  
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44 126 of their surface modifications. The research projects described in this review were then selected by  
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47 127 using three successive filters: firstly, *surface topography* approaches over the last 5 years were  
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50 128 explored. Secondly, the articles in which *surface chemistry* was used to complement the *surface*  
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54 129 *topography* were isolated. And thirdly, only the works that exposed the engineered surfaces to  
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4 130 biomolecular and/or micro-organisms fouling were selected. Even if they can be sometimes a  
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7 131 source of inspiration for developing antibiofouling surfaces, research topics such as anti-corrosion  
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10 132 or self-cleaning surfaces, were mainly left aside.

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14 133 The in-depth analysis of the selected works led to several levels of classification following a  
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18 134 bottom-up process, as detailed in Figure 2. The first one is the nature of the substrate that is to be  
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21 135 provided with antibiofouling property: metals and their oxides and hydroxides, glass and silicon-  
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24 136 based materials, and polymers. Secondly, the articles are classified depending on the method used  
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28 137 to tune the substrate topography (step 1), either by modifying the substrate itself (endogenous  
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31 138 topography), or by using an additive strategy and adding another material (exogenous topography).  
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34 139 The third level relates to the surface chemistry modification: a vast majority of approaches  
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38 140 complement the topography with a chemical layer (step 2), but some approaches simultaneously  
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41 141 tune the substrate topography while producing the chemical layer (step 1&2).  
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142  
143 *Figure 2: Combining topography and chemistry to obtain antibiofouling surfaces on different substrates*  
144 *(metals, glass and silicon, polymers). The first step consists in designing regular or random topography. In*  
145 *the second step a specific chemistry is added. It is also possible to obtain topography simultaneously with*  
146 *the surface chemistry modification process. In the next figures, the blue overlay will indicate the*  
147 *topography design, while the green overlay will indicate the chemistry modification.*

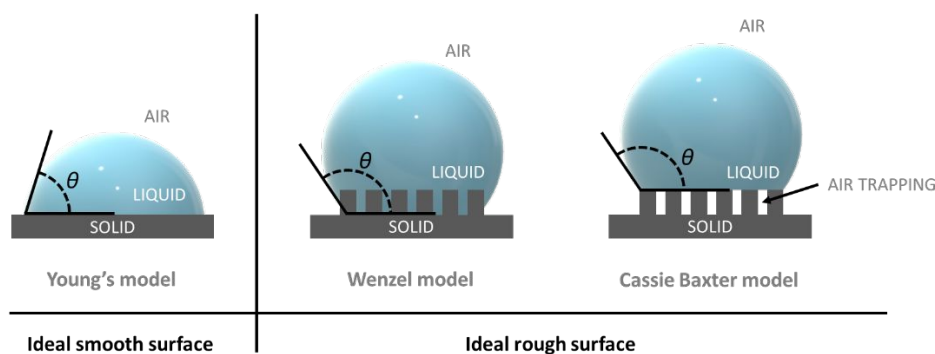
148 Whatever the approach the resulting engineered surface from the combination of topography and  
149 chemistry will either fall into hydrophilic or hydrophobic surface. For hydrophobic approaches a

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4 150 very limited amount of chemical entities are used: fluorine-based moieties and alkyl chains have  
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7 151 been used for a long time in order to produce hydrophobic and superhydrophobic surfaces. More  
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10 152 recently, surfaces infused with silicon oils have been developed and used as self-cleaning surfaces  
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13 153 (often referred as slippery liquid infused surfaces, SLIS). Some research teams also used them in  
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17 154 antibiofouling applications. Conversely, for hydrophilic approaches, chemical entities are  
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20 155 numerous as exposed on Figure 2. Ranging from simple functional groups such as amine or  
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23 156 carboxylic acids to polymers and ionic compounds, hydrophilic approaches are at the heart of  
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27 157 today's most innovative antibiofouling research works. This manuscript is thus separated into two  
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30 158 chapters, the first one detailing the hydrophobic approaches, and the second one focusing on the  
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33 159 hydrophilic ones. This review is written from an applicative engineer perspective, the sub-chapters  
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36  
37 160 are thus organized according to the nature of the surface to be treated: metals, glass and silicon-  
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39  
40 161 based or polymers. The conclusion and outlook will provide the reader with recommendations  
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42  
43 162 regarding further development of antibiofouling surfaces.

## 44 45 46 47 163 **2. Combined topography and hydrophobicity for adhesion prevention**

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50  
51 164 A majority of topographical hydrophobic approaches use fluorine-based compounds as a chemical  
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55 165 layer to increase the hydrophobicity. This is why the subchapter will not be organized regarding  
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4 166 the type of chemistry used on the engineered surface but rather according to the method of  
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7 167 designing the topography: endogenous, exogenous or a combination of both, as detailed on Figure  
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10 168 2. Whatever the method, the same objective remains: decrease the contact area between the surface  
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13 169 and the liquid medium in order to prevent fouling interactions with biomolecules or micro-  
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17 170 organisms. As described in Figure 3, different models of surface wetting have been developed and  
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19  
20 171 are widely discussed in the literature.<sup>28,29</sup> The Cassie-Baxter regime is predominantly cited in this  
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22  
23 172 sub-chapter since it is the best way to prevent the liquid from fully wetting the surface. This regime  
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26  
27 173 is almost exclusively reached when a hydrophobic chemical entity is used in combination with the  
28  
29  
30 174 topography design.



175  
176 *Figure 3: Surface wetting regimes and contact angle  $\theta$  measurements on ideal smooth surfaces and*  
177 *rough surfaces.*

178 In this chapter, only the production technique of the topographical features really differs from one  
179 study to another. This angle is going to lead our story for each category of substrate: metals, silicon-

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4 180 based samples and polymers. In addition, a few studies introduce approaches that are compatible  
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7 181 with various substrate types. A specific subchapter is dedicated to them. All the approaches are  
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10 182 detailed in Table S2 of the Supplementary information.

## 14 183 **2.1. Metallic substrates**

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17 184 Metallic surfaces that are potentially exposed to biofouling are encountered in various fields of  
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21 185 activity, such as marine industry, food preparation facilities and healthcare.

### 24 186 **2.1.1. Endogenous topography: micro/nanostructure designed from the** 25 26 187 **metallic substrate**

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30 188 In order to tune the topography, the most straightforward methods rely on the direct modification  
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33 189 of the metals surface itself. Micro/nanostructure can be produced through different approaches of  
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36 190 aqueous phase treatments and etching techniques which provide the surface with engineered  
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40 191 topography. These micro/nanostructures are referred as endogenous topographies.

#### 43 192 **2.1.1.1. Aqueous phase treatment**

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46 193 A simple way to modify the topography of metallic substrates is the formation of oxide and  
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50 194 hydroxide layers at their surface. Upon immersion in boiling water, acidic or alkaline solutions or  
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53 195 a combination of these, metallic oxides, that are produced at the surface of the substrates, form

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4 196 hierarchical structures. Aluminium, magnesium or copper substrates are predominantly represented  
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7 197 in the following reviewed articles. Using a subsequent step of chemical surface modification with  
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10 198 hydrophobic compounds, some research teams managed to use combined topographical and  
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13 199 chemical approaches to obtain superhydrophobic substrates. For instance, commercial aluminium  
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17 200 sheets were enhanced with hierarchical micro/nano topographies produced by strong acid etching  
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20 201 followed by immersion in boiling water. Subsequently, 1H,1H,2H,2H-  
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23 202 perfluorodecyltrichlorosilane also known as FDTTS was used to chemically functionalize the  
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27 203 structured Al surfaces, as depicted on Figure 4A.<sup>30</sup> During boiling water treatment, the average  
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30 204 roughness increased from 5 to 65 nm with the formation of Bohemite under the form of  
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33 205 nanoplatelets on top of the existing microprotusions. Only the combination of micro and nanoscale  
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37 206 roughness with hydrophobic silane grafting provided the surface with superhydrophobic properties  
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40 207 which resulted in a drastic decrease of bovine serum albumin (BSA) adsorption. An 80% relative  
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43 208 reduction in adhered bacteria was measured, regardless of the bacterial strain and their outer layer  
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47 209 properties (*Pseudomonas aeruginosa*, *Staphylococcus epidermidis*, and *Staphylococcus aureus*).  
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50 210 Finally, cytotoxicity of the samples was assessed through MTT assay and relative complete cell  
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53 211 compatibility (HeLa cells) was validated, confirming the benefits of such a treatment for *in vivo*



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4 212 applications. More recently, Mandal and co-workers studied the modification of an aluminium  
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7 213 alloy through micro-imprinting to obtain square micropillars, followed by hot water treatment  
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10 214 which covered the pillars with flake-like AlO(OH) bohemite nanostructures. Finally, a perfluoro-  
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13 215 silane layer was deposited by chemical vapor deposition (CVD) on top on the nanostructure. The  
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17 216 superhydrophobic Cassie-Baxter regime was achieved and allowed for a drastic decrease of  
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20 217 *Escherichia coli* growth.<sup>31,32</sup>  
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24 218 Copper hydroxide can also be produced to tune the surface topography. A copper mesh was  
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28 219 modified through the formation of Cu(OH)<sub>2</sub> nanowires at its surface, followed by Cu based metallic  
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31 220 organic framework (MOF) production and finally polydimethylsiloxane (PDMS) deposition on the  
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33  
34 221 micro/nano structure as depicted in Figure 4B. Hierarchical mushroom-like structures were  
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38 222 obtained as confirmed by scanning electronic microscopy (SEM) images. Water contact angles  
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41 223 above 150° and sliding angles below 4° were measured. Antifouling and self-cleaning properties  
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43  
44 224 were validated against products such as, milk, coffee, tea, cola and juice. In addition, dirt and salts  
45  
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48 225 were easily removed from the substrate leaving no trace. But more importantly, drag reduction also  
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51 226 benefited from the treatments applied to the Cu mesh, making it a promising material for innovative  
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54 227 marine vehicle development.<sup>33</sup>  
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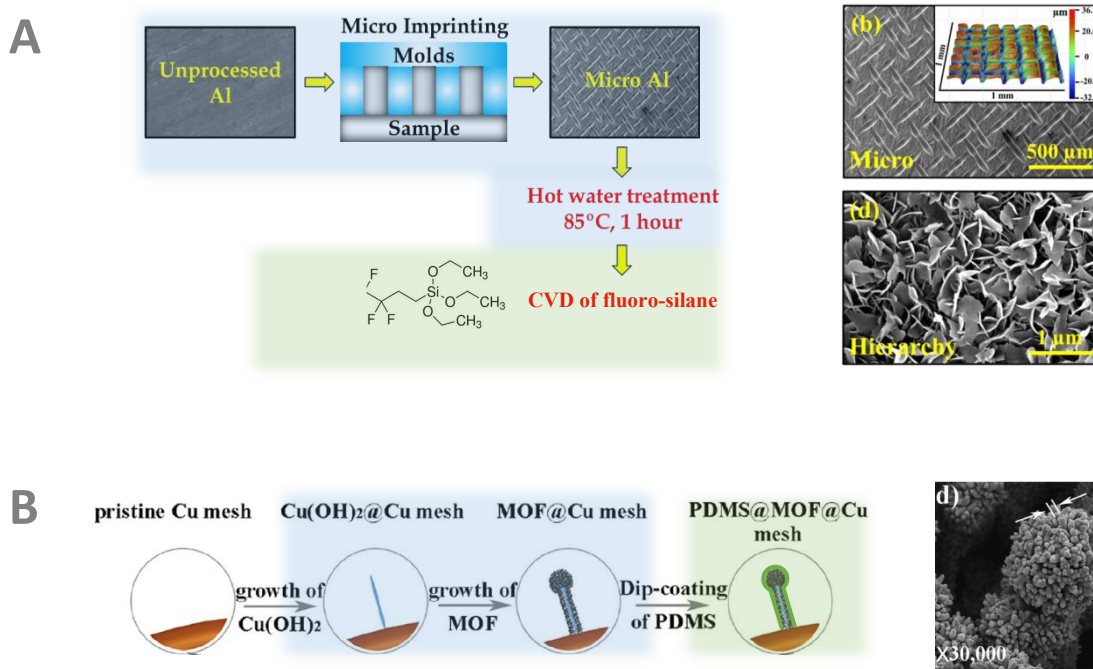


Figure 4: Combined approaches using metal oxide and hydroxide for topography design and detailed surface chemistry adopted. A: Imprinted aluminum micro-pillars covered with bohemite obtained by hot boiling water treatment, followed by FOTES CVD (adapted with permission from reference <sup>32</sup>, Copyright 2022 Elsevier), B: super-hydrophobic PDMS/metal-organic-framework copper mesh (adapted with permission from reference <sup>33</sup>, Copyright 2011 Elsevier). Blue and green overlay indicate topography and chemistry modifications, respectively.

### 2.1.1.2. Laser etching

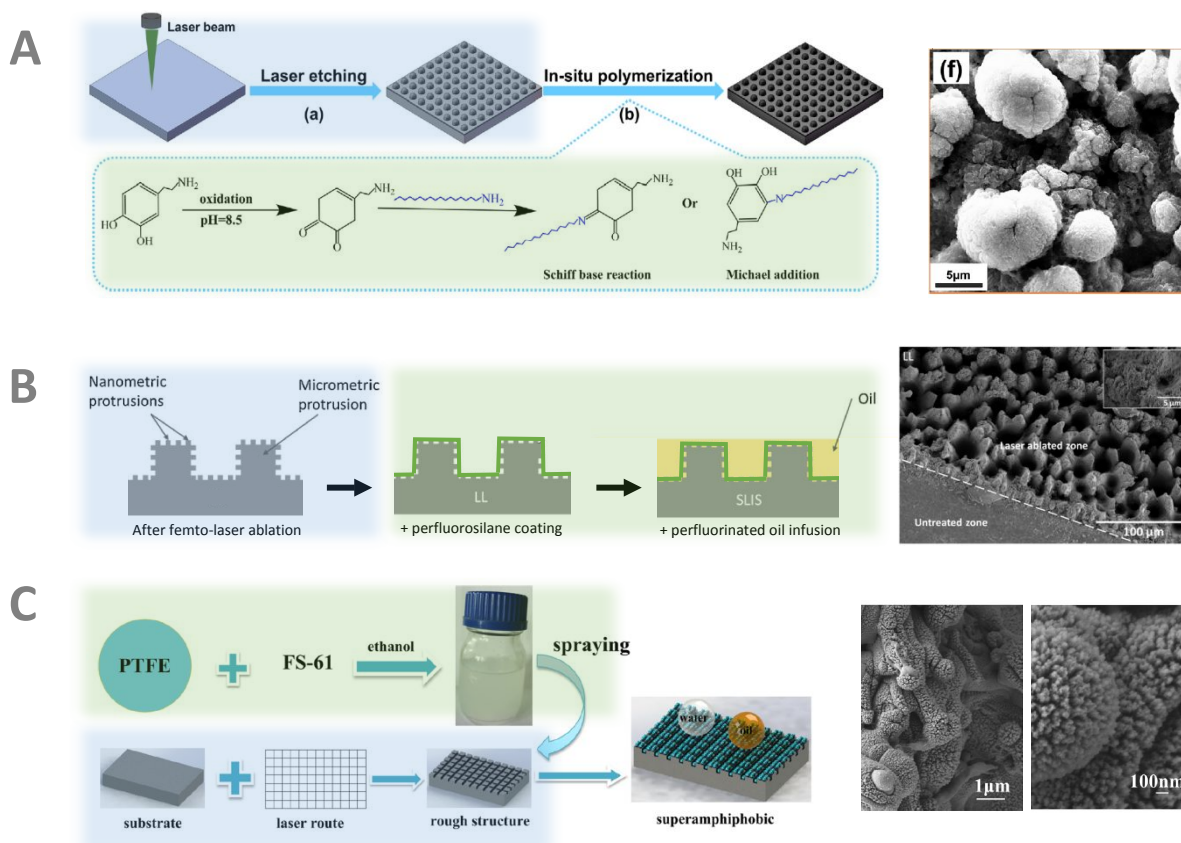
Laser-based techniques are highly represented for modifying metals' topography.<sup>34,35</sup> Aluminium and stainless steel substrates are easily modified with this technique. For instance, Li *et al* used Laser Interference Patterning on stainless steel to create micro and nano structures mimicking the gecko surface.<sup>36</sup> This surface patterning created superhydrophilic substrates with a water contact angle (WCA) close to 0°, in accordance to the Wenzel model (Figure 3). However, the following *in situ* polymerisation of a mixture of polydopamine and octadecylamine monomers led to the

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4 243 formation of small flocules and a WCA of 157.3°, confirming superhydrophobicity (see Figure  
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7 244 5A). A 1-log reduction of bacterial growth was observed for *E. coli* (about 90% inhibition), a 2-  
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10 245 log reduction was obtained against *S. aureus*, for which an inhibition efficacy of over 99% could  
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13 246 be observed. The difference in bacterial membrane structure between Gram positive and Gram  
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17 247 negative is used to explain this result. To assess the long-term use of these substrates, abrasion  
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20 248 tests were carried out with sandpaper, and 6-month storage in air also took place. Neither of these  
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24 249 experiments considerably affected the properties of the surfaces.

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28 250 Taking inspiration from lotus leaves, Zouaghi and co-workers used femtosecond laser ablation onto  
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30  
31 251 stainless steel surface to produce micro and nano topography. Here, the surface was coated with a  
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34 252 perfluorosilane in an organic solvent, resulting in a first combined approach called LL (lotus-  
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37  
38 253 like).<sup>37</sup> A second approach consisted in impregnating this LL substrate with an perfluorinated oil  
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41 254 in order to obtain a slippery liquid infused surface (SLIS) also known as SLIPS (for slippery liquid  
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45 255 infused porous surface), as depicted in

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48  
49 256 Figure 5B. Antibiofouling tests were performed in a pilot pasteurizer with a model fluid composed  
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52 257 of 1 wt% of whey protein, in a temperature range representing dairy industry conditions (65-85°C).  
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56 258 Although a complete suppression of fouling was observed for SLIPS, an increase in fouling was

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4 259 detected for LL. The wide open topography of LL substrates explained the fouling increase, large  
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7 260 and deep holes of *ca.* 10 to 20  $\mu\text{m}$  were easily filled by foulants and the role of chemical layer was  
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9  
10 261 impeded, as explained by the authors.<sup>38</sup> The SLIPS substrate benefited from the infused  
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13 262 hydrophobic oil which behaved like a smooth liquid surface. However, the SLIPS approach failed  
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17 263 durability testing after only one cycle in the pasteurizer. An optimized topography to increase oil  
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20 264 retention and the use of an alternative oil more suitable to the food industry are cited as  
21  
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24 265 perspectives.



266

267 *Figure 5: Combined approaches using laser techniques for topography design and detailed surface*  
 268 *chemistry adopted. A: Laser Interference Patterning on stainless steel, followed by polymerization of*  
 269 *octadecylamine and polydopamine (adapted with permission from reference <sup>36</sup>, Copyright 2019 Elsevier).*  
 270 *B: femtosecond laser ablation onto stainless steel followed by perfluorosilane coating and perfluorinated*  
 271 *oil infusion (adapted with permission from reference <sup>38</sup>, Copyright Elsevier 2019).*  
 272 *C: UV laser etching on aluminum and stainless steel, coated with PTFE nanoparticles (adapted with permission from reference*  
 273 *<sup>39</sup>, Copyright 2021 Elsevier). Blue and green overlay indicate topography and chemistry modifications,*  
 274 *respectively.*

275 Ultraviolet (UV) laser etching was also used on aluminium and stainless steel metallic substrates  
 276 to produce topographic features following vertical and horizontal lines with 30 μm spacing. Then,  
 277 a coating composed of polytetrafluoroethylene (PTFE) nanoparticles and surfactant was sprayed  
 278 with N<sub>2</sub> gas onto the etched metallic surfaces, before a final thermal treatment (Figure 5C). SEM

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4 279 imaging revealed the micro and nano-sized topographical features. Chemical characterization with  
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7 280 energy dispersive spectroscopy confirmed the homogeneous covering with the spraying technique.  
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10 281 The wettability was evaluated against several different liquids (water (pH 0 and 14), ethanol  
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13 282 solutions, rapeseed oil, ethylene glycol, propylene glycol and cyclohexane) that all reached contact  
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17 283 angles above 150°, confirming superamphiphobic properties. The combination of surface  
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19  
20 284 topography and hydrophobic chemistry leads to antifouling properties and has potential drag-  
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23  
24 285 reduction properties. Moreover, the mechanical robustness of the coating was confirmed after  
25  
26  
27 286 abrasion tests which led to a very small loss of super-amphiphobic properties. The micro  
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29  
30 287 topography withstood the abrasion and both nano topography and chemical functions were  
31  
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33  
34 288 preserved.<sup>39</sup>

### 37 289 **2.1.1.3. Reactive ion etching**

40 290 Reactive ion etching (RIE) was implemented on stainless steel by Cao and co-workers to produce  
41  
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44 291 rectangular micropillars with different arrangements and spacing. A peptide coating was applied  
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46  
47 292 through immersion, and resulted in a hydrophobic surface that decreased the adhesion of marine  
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50 293 algae *Chlorella pyrenoidosa* and *Phaeodactylum tricornutum*. The synergy between topography  
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54 294 and chemical peptide layer was confirmed.<sup>40</sup> High power electro-etching in sodium chloride  
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4 295 solution has also been used to produce micropillars on stainless steel surface, followed by vapor  
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7 296 deposition of various FDA-approved food-contact coatings: Ni-P-PTFE, Lectrofluor® 641, CrN,  
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10 297 TiN, and Dursan®. Among them, the patented Dursan® coating process offered the most  
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13 298 promising fouling resistance against *L. monocytogenes*, but the combination with micropillars gave  
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17 299 roughly the same results as on flat samples.<sup>41</sup>  
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## 21 300 2.1.2. Exogenous topography: micro/nanostructure through additive 22 23 301 strategies on metals 24 25

26 302 Additive strategies give access to more diverse topography geometries. By incorporating various  
27  
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29 303 micro or nano objects to the metallic surface, some research teams developed antibiofouling  
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33 304 surfaces with more complex topographies. These are referred to as exogenous topographies.  
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### 36 305 2.1.2.1. Electro-deposition. 37 38

39 306 By using a metallic substrate as an electrode, electro-deposition of diverse conducting substances  
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43 307 can be achieved. For instance, using copper foil as an electrode exposed to a phosphate containing  
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46 308 electrolyte, Bao *et al*/produced microflower-like structures composed of copper and phosphate ions  
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49 309 complexes. Although no biological anti-fouling experiments were conducted, a superhydrophobic  
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53 310 self-cleaning and anti-corrosion surface was obtained after dodecylamine coating.<sup>42</sup> Inspired by  
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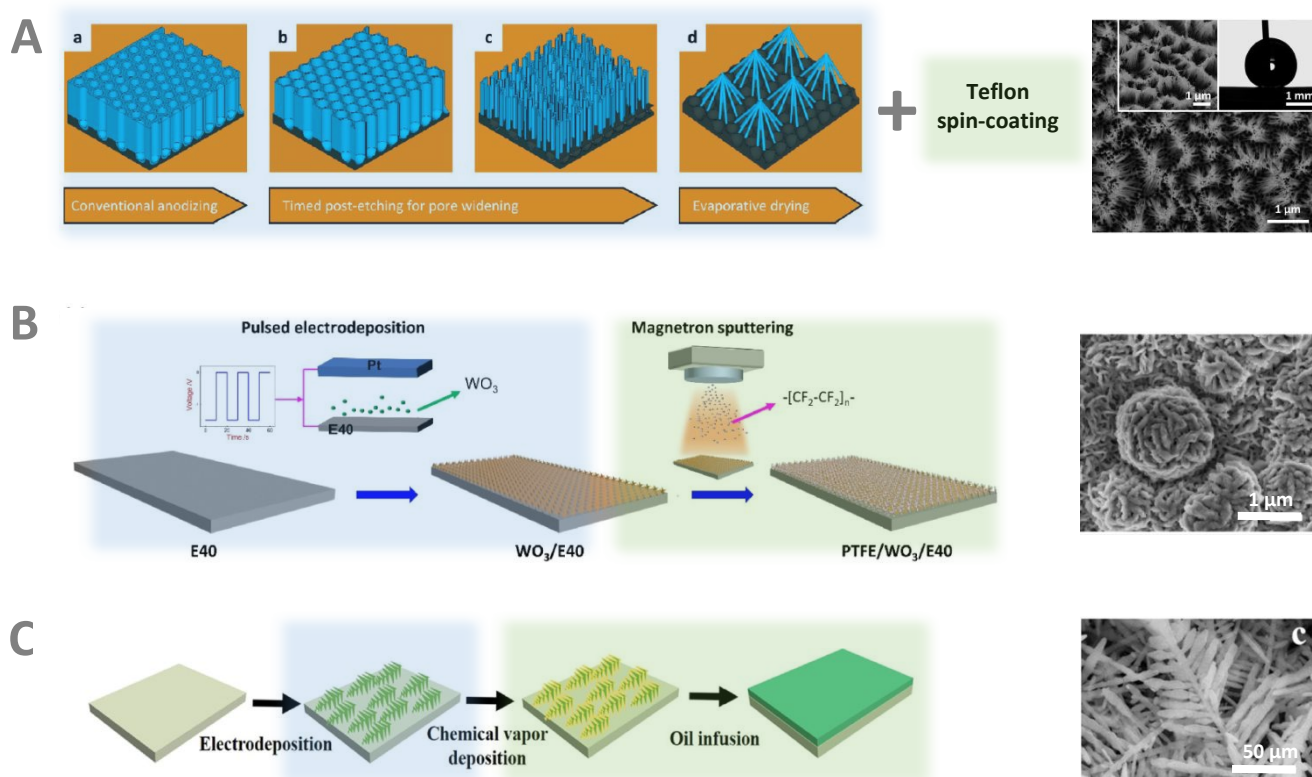
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4 311 similar research,<sup>43,44</sup> the team of Chang-Hwan Choi chose aluminium foil to be anodized in an  
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7 312 oxalic acid solution to obtain a nanoporous structure that was thinned down with phosphoric acid  
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10 313 treatment, resulting in disconnected nanopillars. After evaporation under controlled conditions,  
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13 314 clusters of nanopillars assembled into conical nanostructures. A Teflon<sup>TM</sup> coating was finally  
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17 315 applied to obtain a superhydrophobic surface (Figure 6A) which was submitted to biofouling tests  
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20 316 against *E. coli* and *S. aureus* in static and dynamic conditions.<sup>45</sup> Up to 4-log reductions were  
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23 317 obtained upon bacterial adhesion testing for conical pillars covered with Teflon<sup>TM</sup> only, confirming  
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27 318 the synergy between the nanotopography and surface chemistry. A more recent study used  
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30 319 Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O electrolyte to create flower-like nanosheets through electro deposition onto  
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33 320 polished E40 steel. The treatment was followed by high vacuum sputtering of PTFE and resulted  
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37 321 in a superhydrophobic micro/nano structured PTFE/WO<sub>3</sub> coated E40 steel substrate (Figure 6B)  
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40 322 with anti-pollution, anti-icing and antibiofouling properties (also obtained on Cu, Mg and Ti  
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43 323 alloys). *Shewanella algae* adhesion was completely avoided over 14 days immersion in the bacterial  
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47 324 suspension, while raw E40 steel and PTFE coated steel were covered with bacteria. The  
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50 325 superhydrophobicity and electrostatic repulsion arising from the synergistic combination of  
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53 326 micro/nano-structure and PTFE coating are believed to explain such results.<sup>46</sup> However, the WO<sub>3</sub>



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4 327 coated-only steel was not part of the antifouling characterized samples. It could have helped to  
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7 328 better distinguishing contributions of micro/nano-structure *vs* chemical surface composition for  
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10 329 explaining antibiofouling results. Ouyang and co-workers grew dendritic Ag micro/nanostructures  
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13 330 through Ag electro-deposition onto Titanium substrates, followed by dodecanethiol vapor  
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17 331 deposition and dimethyl silicone oil infusion to produce a Slippery Liquid-Infused Porous Surface  
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20 332 (SLIPS) (Figure 6C). A reduction by 4 orders of magnitude of diatom *Navicula minima* and green  
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24 333 algae *Chlorella vulgaris* was achieved upon 14 days of incubation.<sup>47</sup>  
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335 *Figure 6: Combined approaches using electro-deposition based methods for topography design. A:*  
 336 *clusters of nanopillars assembled into conical nanostructures obtained from anodization of aluminum foil*  
 337 *and phosphoric acid treatment with a Teflon™ top layer (adapted with permission from reference*<sup>45</sup>  
 338 *Copyright 2017 American Chemical Society). B: flower-like nanosheets produced with Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O*  
 339 *electrolyte on polished steel, covered with PTFE sputtered layer (adapted with permission from reference*<sup>46</sup>  
 340 *, Copyright 2022 Elsevier). C: liquid-infused superhydrophobic dendritic silver matrix on titanium*  
 341 *(adapted with permission from reference*<sup>47</sup>*, Copyright 2019 Elsevier). Blue and green overlay indicate*  
 342 *topography and chemistry modifications, respectively.*



343 Beyond electrolyte-based electro-deposition treatments, it is also possible to coat conductive

344 polymers and obtain an antibiofouling effect. Stainless steel surfaces were turned

345 superhydrophobic by electrodeposition of hydrophobic and conducting poly(3,4-

346 ethylenedioxythiophene) (PEDOT) under the form of nanofibers.<sup>48</sup> Bacterial adhesion and biofilm

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4 347 growth were investigated against *Pseudomonas aeruginosa* PAO1 and *Listeria monocytogenes* CIP  
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7 348 103574 (commonly found in medical facilities and food industry environments). The smallest value  
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10 349 of deposition charge (1 mC.cm<sup>-2</sup>, without nanofibers), did not reduce the bioadhesion. On the  
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13 350 contrary, higher deposition charge (35 mC.cm<sup>-2</sup>), producing expanding vertical nanofibers, reduced  
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17 351 the bioadhesion by 3-4 log. This result confirmed that the superhydrophobic chemistry alone was  
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20 352 not enough to reduce the bacterial bioadhesion. A prominent surface topography was necessary to  
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23 353 achieve bacterial adhesion reduction. Biofilm growth was also performed and biofilm biovolume  
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27 354 were measured. The same conclusions arised on the importance of surface topography to limit  
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30 355 biofilm development.

#### 34 356 **2.1.2.2. Other methods**

35  
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37 357 Leaving aside electro-deposition, the next three articles use different exogenous methods to create  
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40 358 topography. The first approach relies on the production of layered double hydroxide (LDH) films.  
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43 359 Aluminium alloys were coated with lithium-aluminium (Li-Al) LDH films. This is known as  
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47 360 hydrotalcite preparation. The samples were functionalized with 4-amino-2-((hydrazine methylene)  
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50 361 amino)-4-oxobutanoic acid (AOA) and 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane (PFOTES).  
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54 362 This method produced films with hydrophobicity, antibiofouling and anti-corrosion properties.<sup>49</sup>  
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4 363 SEM analysis showed a nest-like rough structure for these films with vertically-grown crosslinked  
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7 364 nanoplates. These films showed good anti-adhesive properties towards *E. coli*, *Bacillus subtilis* and  
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10 365 sulfate reducing bacteria, with repellency over 96% for each species. Antibacterial activity against  
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13 366 Gram-positive, Gram-negative and anaerobic bacteria is provided by the guanadino group of the  
14  
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17 367 AOA. Combined with the surface roughness and hydrophobicity, this leads to surfaces with high  
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20 368 antibiofouling capacities. Using atmospheric pressure plasma spraying (APPS), the liquid  
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23 369 precursor hexamethydisiloxane was deposited onto foodgrade stainless steel. Process parameters  
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27 370 were studied in a first paper which revealed the influence of the precursor flow on the surface  
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30 371 roughness and morphology of the resulting coated surface (denoted as PL).<sup>37</sup> This refers to the *Step*  
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33 372 *1&2 Simultaneous topography and chemistry* approach described on Figure 2. The particular  
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37 373 chemical surface composition, combined with the random nanostructures revealed by atomic force  
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40 374 microscopy (AFM), led to a strong reduction of fouling upon two consecutive runs in a pilot  
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44 375 pasteurizer. A second study was conducted to compare this PL sample with lotus-like (LL) and  
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47 376 SLIPS samples that were described earlier in the previous *endogenous* section. Upon the fouling  
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50 377 test in the pasteurizer, LL and SLIPS surfaces failed to overcome the durability of PL surfaces over  
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54 378 the two consecutive runs.<sup>38</sup> Different bacterial strains were tested on PL samples only and  
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4 379 compared to bare stainless steel surface: a very mild reduction of *S. aureus* adhesion was observed,  
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7 380 but a strong reduction of bacterial adhesion for rod-shaped bacteria was obtained: 58% and 80%  
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10 381 for *L. monocytogenes* and *Salmonella enterica* respectively. The round-shaped bacteria are able to  
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13 382 penetrate into the microspaces of the grain structures of the PL surface, while rod-shaped bacteria  
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17 383 cannot, and thus have less anchoring spots, leading to reduced adhesion. However, authors did not  
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20 384 discuss the viable or dead state of the adhered bacteria that usually allow for further understanding  
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24 385 of the anti-adhesion and/or contact bactericidal effect.

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28 386 Finally, Selim and co-workers used alumina or zinc nanorods associated with PDMS on steel in  
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31 387 order to fight against marine fouling. In a first study, graphene oxide-alumina nanorod hybrid  
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34 388 sheets were enhanced with exfoliated PDMS chains. The optimal amount of 1 wt% nanofiller  
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38 389 ensured the best dispersion of the nanoparticles. The resulting coating exhibited  
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41 390 superhydrophobicity and fouling resistance. After 28 days *in vitro* exposure to *Micrococcus sp.*  
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44 391 (Gram-positive), *Pseudomonas putida* (Gram-negative) or *Aspergillus niger* (fungus), a sharp  
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48 392 reduction of cell viability was observed. Fouling resistance was also confirmed with a three-month  
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51 393 field assay in marine waters.<sup>50</sup> In another study, zinc oxide nanorods were embedded in a PDMS  
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55 394 matrix to produce a similar superhydrophobic coating on steel. The same bacteria and fungus were

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3 395 used for fouling resistance tests and, again, an optimized amount of nanofiller was detected at 0.5%  
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7 396 above and below which the properties were lost. A 6-month field trial assay in natural seawater  
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10 397 confirmed the *in vitro* tests. In both of these studies, the micro/nano-roughness combined to low  
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13 398 energy surface chemistry is called to explain the results.<sup>51</sup>  
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## 17 399 **2.2. Glass and silicon substrates**

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20 400 Regarding glass and silicon substrates, fewer articles dealing with combined topography and  
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23 401 chemistry approaches were encountered. The first one uses endogenous topography, produced  
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26 402 through laser patterning, while the second one uses both endogenous (reactive ion etching) and  
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30 403 exogenous topography with addition of another material (crystal seeding). All the others use  
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33 404 different exogenous topographies.  
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38 405 Lee *et al* addressed biofouling on endoscope lenses. In order to prevent bacterial infection and  
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41 406 fogging while achieving high mechanical durability, the lens was provided with a lubricant-infused  
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44 407 directly engraved nano/micro-structured surface (LIDENS).<sup>52</sup> Femtosecond laser patterning was  
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47 408 first applied to the devices to obtain nanostructured surfaces. A coating of fluorinated self-assembly  
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51 409 monolayer was then added before infusion of the perfluorocarbon-based lubricant whose affinity  
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54 410 with the surface is increased with the fluorocarbon chains (see Figure 7A). The LIDENS coating  
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4 411 showed very good anti-adhesive effects towards blood which rolled off the surface without leaving  
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7 412 any trace. Fluorescent microscopy also demonstrated low adhesion towards albumin and  
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10 413 fibrinogen. In addition, tape-peeling and linear abrasion tests confirmed the robustness of the  
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13 414 LIDENS coating.

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17 415 The next approach engraved the raw substrate to create micro-topography (endogenous), but also  
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21 416 used a new material to produce the nano-topography on top of it (exogenous). Inspired by the lotus-  
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24 417 leaf effect, silicon wafers were subjected to RIE to produce micro-cylinders. Zinc oxide crystal  
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28 418 seeds were then spincoated onto the microstructured surface allowing for the growth of Zinc salt  
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31 419 nanoneedles through low temperature hydrothermal reaction. Finally, a fluoroalkylsilane coating  
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34 420 was deposited by immersion in the silane solution, as depicted in Figure 7B. The resulting surface  
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38 421 exhibited superhydrophobicity with the Cassie-Baxter regime upon contact with liquid. A 99%  
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41 422 bacterial repellency was obtained even after 24h exposure to a bacterial suspension of *E. coli*,  
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44 423 compared to the flat untreated silicon wafer.<sup>53</sup> Moreover, the few bacteria that eventually adhered  
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48 424 onto the substrates were easily killed by the nanoneedles, as confirmed by their shrunken  
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51 425 morphologies (obtained by SEM) and non-viable state (by live/dead™ staining). The combination  
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of a topographical approach and relevant chemical surface treatment produced a synergistic  
antibacterial solution.

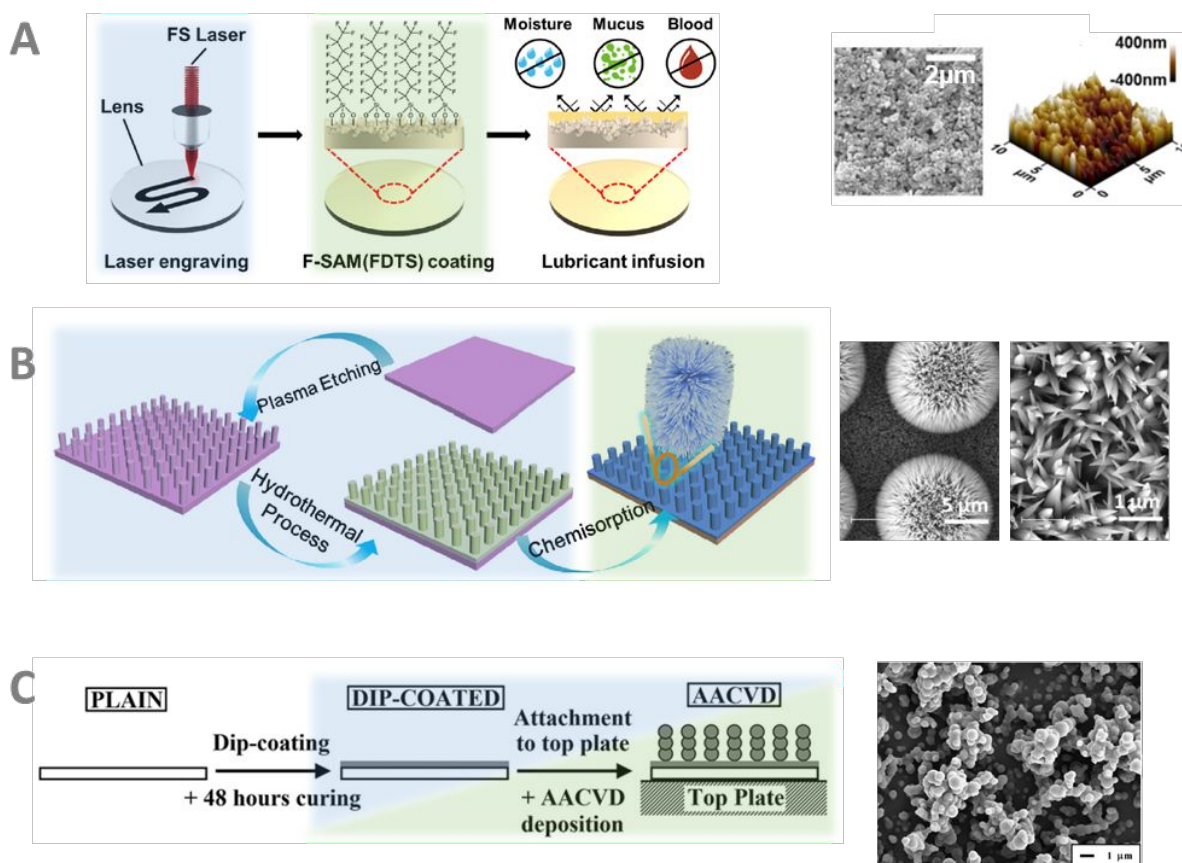


Figure 7: Combined approaches on glass and silicon-based substrates. A: endoscope lens with micro/nanostructure produced by femto-second laser ablation, covered with a fluorinated silane and infused with a perfluorocarbon-based lubricant (adapted from reference <sup>52</sup>). B: micro-cylinders produced by etching of silicon wafer and covered with zinc salts nanoneedles coated with a fluoroalkylsilane (adapted with permission from <sup>53</sup>, Copyright 2020 Elsevier). C: glass slides covered with a silicone elastomer and aerosol assisted chemical vapor deposition (adapted with permission from <sup>54</sup>, Copyright 2011 Elsevier). Blue and green overlay indicate topography and chemistry modifications, respectively.

In the following articles, exogenous materials are introduced to design both the topography and the chemistry.



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4 438 Silane chemistry is of primary interest when silicon-based substrates are to be chemically modified.

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7 439 Privett *et al* used nanostructured fluorinated silica colloids, fluoroalkoxysilane (heptadecafluoro-

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10 440 1,1,2,2-tetrahydrodecyl)-trimethoxysilane (17FTMS) and methyltrimethoxysilane (MTMOS) to

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13 441 develop superhydrophobic xerogel coatings which showed anti-adhesive properties towards *S.*

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17 442 *aureus* and *P. aeruginosa*.<sup>55</sup> The particles showed both micro and nanoscale size. Acid-catalysed

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20 443 hydrolysis and condensation was then performed to obtain 17FTMS/MTMOS films with or without

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23 444 particles. The synergic combination of colloids and the fluorinated xerogel resulted in a

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27 445 superhydrophobic surface. Soaking in water over 15 days did not affect the WCA, suggesting the

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30 446 coatings were stable. These surfaces reduced bacterial adhesion by 99% for *S. aureus* and 98.2%

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33 447 for *P. aeruginosa*.

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37 448 In addition to liquid phase chemistry, vapor phase approaches were also used to tune silicon-based

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40 449 substrates. Hence chemical vapor deposition techniques are able to bring both the topography and

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43 450 the chemistry. In the first example, glass slides were covered with a silicone elastomer film through

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47 451 dip-coating and subsequent aerosol assisted chemical vapor deposition (AACVD) of Sylgard® 184

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50 452 silicon elastomer.<sup>54</sup> This process allowed for the formation of micro-scale random topographic

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54 453 features, as described in Figure 7C. The bacterial adhesion on modified glass slides was evaluated

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4 454 with *E. coli* and *S. aureus* through live/dead™ staining assay in 30 ml of 10<sup>7</sup> colony forming unit  
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7 455 (CFU)/ml bacterial suspensions, maintained for 1 hour in static conditions. Non-adherent bacteria  
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10 456 were then removed and *BacLight*™ Bacterial Viability Staining kit was used to detect adhered  
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13 457 bacteria with fluorescence microscopy. The total amount of live and dead adhered bacteria was  
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17 458 drastically decreased on the modified glass slides, presumably because the aqueous bacterial  
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20 459 suspension is repelled by these surfaces.

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24 460 An atmospheric plasma polymer coating was used to treat silicon wafers and produced a  
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28 461 microstructured topography while also imparting hydrophobic and superhydrophobic properties to  
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31 462 the surface, that prevent bacterial adhesion.<sup>56</sup> A mixture of docecyl acrylate and 1*H*,1*H*,2*H*,2*H*-  
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34 463 perfluorodecyl acrylate precursor was used. AFM imaging revealed a heterogeneous globular grain  
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38 464 structure. The wettability was studied with contact angle measurements to monitor the transition  
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41 465 from hydrophobic Wenzel regime to superhydrophobic Cassie-Baxter regime. The core of the  
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45 466 study lies in the fact that the authors performed statistical analysis to compare the influence of  
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48 467 different parameters on bacterial adhesion. These parameters were either related to the surface  
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51 468 (topography, chemistry, wettability) or to the bacterial medium in which the substrate was  
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55 469 incubated (bacteria species, culture, medium composition). The main result indicated that bacterial  
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4 470 colonization is by far predominantly influenced by culture conditions rather than surface properties.  
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7 471 This input is precious for researchers that tackle antibiofouling surface development since it  
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10 472 encourages them to use various medium conditions to assess precisely the antibiofouling  
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13 473 properties. The second result indicates that the superhydrophobic substrates were the more  
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17 474 effective at preventing bacterial adhesion, even after static or hydrodynamic long term culture. This  
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20 475 type of statistical analysis of the influence of culture conditions could be done for every type of  
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24 476 surface treatment that is developed to fight bacterial fouling.  
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## 27 477 **2.3. Polymer substrates**

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30 478 As for a few of the metallic substrates, the following approaches dealing with polymeric substrates  
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34 479 can be separated into endogenous and exogenous topography. Molding techniques and plasma  
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37 480 treatments are highly represented in the former category, while co-polymers and inorganic  
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41 481 structures are used in the latter to design the topography.  
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### 44 482 **2.3.1. Endogenous topography: micro/nanostructure designed from** 45 46 483 **polymers**

#### 47 48 49 484 **2.3.1.1. Molding**

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52 485 Polymers are soft matter compared to metal and silicon-derived materials. Topographical features  
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56 486 can thus be easily obtained with simple thermal treatment of molding/templating processes, as it is  
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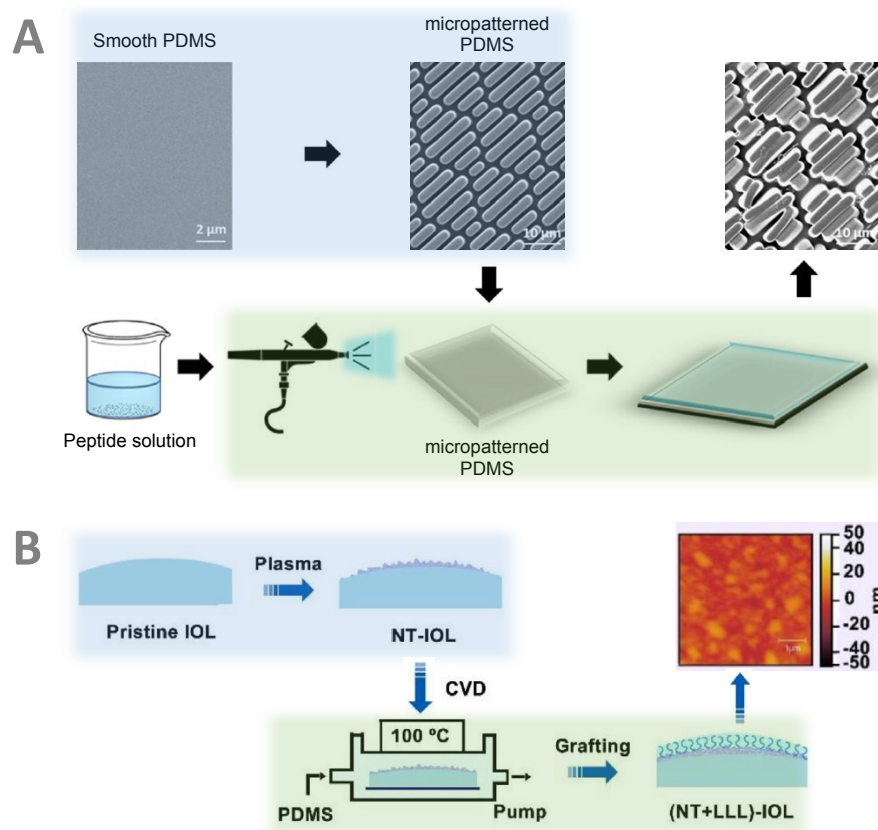
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4 487 described in the next studies. Inspired by the pitcher plant, Ware and co-workers tuned the  
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7 488 topography of Teflon™ coated on polyethylene substrates with a simple thermal treatment at 160°C  
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10 489 to produce micro-wrinkles in which a silicon oil was then infused. The resulting superhydrophobic  
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13 490 surface demonstrated a 99% adhesion inhibition against *Pseudoalteromonas spp.* bacteria. The  
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17 491 inhibition was still above 76% after 2 weeks exposure to seawater. A complementary field test was  
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20 492 performed for 7 weeks in the ocean and the surface was only covered at 23% when reference  
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23 493 samples were fully covered with marine fouling.<sup>57</sup> The article also contains a brief overview of a  
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27 494 dozen studies related to lubricant infused surfaces that were tested against biological foulants such  
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30 495 as bacteria.

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34 496 Dolid *et al* combined a shark-skin pattern on PDMS with a peptide-based coating to obtain  
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38 497 functional surfaces that repel bacteria.<sup>58</sup> A silicon wafer master produced by photolithography was  
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41 498 used to mold the structured shark-skin patterned surface, and a dopamine and peptide-based  
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45 499 mixture was then used to coat the PDMS substrates by a spraying technique, as depicted in Figure  
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48 500 8A. The water contact angle reached 119°. Upon testing against *E. coli* adhesion, it was shown that  
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51 501 the chemically and topographically modified surfaces reduced bacterial adhesion by 85% in  
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55 502 comparison to bare substrates. With *S. epidermidis*, adhesion reduction reached 72%. Dynamic

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4 503 assays were also carried out with *E. coli* and demonstrated that no adhesion occurred on the peptide-  
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7 504 coated and patterned substrates.  
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11 505 **2.3.1.2. Plasma treatment**  
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13 506 Plasma treatment can easily and rapidly modify the topography of polymers. In the next studies,  
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17 507 different plasma treatments are used to modify the topography of polymer substrates. Oxygen  
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20 508 plasma treatment is a very common process and can easily modify polymers' topography. But other  
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23 509 gases are able to form plasma, and their combination with fluorinated carbon compounds lead to  
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27 510 topography modification as well as hydrophobization.  
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511  
 512 *Figure 8: Combined approach with endogenous topography design. A: shark-skin pattern on PDMS with a*  
 513 *peptide-based coating (adapted with permission from reference <sup>58</sup>, Copyright Elsevier 2020). B: intra-*  
 514 *ocular lens with nanotopography produced by oxygen plasma and covered with PDMS brushes to obtain*  
 515 *a liquid-like surface (adapted with permission from reference <sup>59</sup>, Copyright Elsevier 2021). Blue and green*  
 516 *overlay indicate topography and chemistry modifications, respectively.*

517 In order to prevent posterior capsule opacification (PCO) after cataract surgery, caused by adhesion  
 518 of residual lens epithelial cells, researchers from Sun Yat-sen University imparted an intraocular  
 519 lens (IOL) with nanotopography combined with PDMS brushes impregnated with silicon oil.<sup>59</sup> An  
 520 oxygen plasma treatment on the hydrophobic acrylic IOL formed the nanotopography. The PDMS  
 521 brushes were then tethered through a CVD system with the silicon oil (Figure 8B). The free end of  
 522 the grafted polymer chain formed a liquid-like coating. AFM confirmed the superior roughness of

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4 523 the prepared surfaces. The enhanced IOL was also as transparent and mechanically resistant as the  
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7 524 pristine IOL. Anti-bioadhesion and cell viability experiments as well as animal testing  
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10 525 complemented with statistical analysis were performed. Bioadhesion is reduced the most when  
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13 526 topography and the chemical liquid-like layer are used simultaneously. The same outcome was  
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17 527 confirmed for cell viability. After 60 days of *in vivo* experiments, the enhanced IOL demonstrated  
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20 528 excellent biocompatibility and anti-PCO effect.

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24 529 Oxygen plasma micro/nano-texturation was also performed on poly(methyl-methacrylate)  
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28 530 (PMMA) transparent sheets. Combined with metal-sputtering and/or hydrophobic film deposition,  
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31 531 antibiofouling and antimicrobial properties were obtained.<sup>60</sup> Two different hydrophobic coatings  
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34 532 were finally used: octafluorocyclobutane (C<sub>4</sub>F<sub>8</sub>) that was deposited through plasma again, and  
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38 533 perfluorooctyltrichlorosilane (pFOTS) through vapor deposition after oxygen plasma activation.  
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41 534 For this review, the focus here covers only the textured PMMA sheets modified with hydrophobic  
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45 535 coatings only (no metals). These samples were immersed in a bacterial suspension of unicellular  
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48 536 Gram-negative cyanobacteria *Synechococcus sp.* for 72 hours in order to study bacterial adhesion.  
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51 537 A resulting coverage of less than 1.5% was detected, suggesting efficient anti-adhesive properties.  
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55 538 However, the author did not discuss the potential synergistic effect of the micro/nano-texture and  
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4 539 hydrophobic coatings. Experiments with hydrophobic coatings on PMMA without the micro/nano  
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7 540 texture would have helped on this matter.  
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11 541 Argon and Argon/CF<sub>4</sub> plasmas were used to modify polycarbonate substrates. The Argon/CF<sub>4</sub>  
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14 542 treatment imparted both topography and specific surface chemistry that reduced bacterial and  
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17 543 microalgae adhesion.<sup>61</sup> AFM measurements revealed that Ar plasma alone was not able to modify  
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21 544 the polycarbonate substrates topography. Only Ar/CF<sub>4</sub> plasmas increased the roughness  
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24 545 significantly. Bioadhesion tests were performed in flow-cells with bacterial (two Gram negative  
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28 546 marine bacteria, *Paracoccus sp.* 4M6 and *Pseudoalteromonas sp.* 5M6) and diatom (two axenic  
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31 547 microalgae strains, *Cylindrotheca closterium* AC-170 and *Porphyridium purpureum* AC-122)  
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34 548 cultures. Bacteria were exposed 2 h to the surface while 24 h exposure with 12 h-12 h light-dark  
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38 549 cycle was carried out with microalgae. The main outcome is that only the Ar/CF<sub>4</sub> treated  
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41 550 polycarbonate with higher content of CF<sub>4</sub> managed to reduce the adhesion of the tested micro-  
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44 551 organisms (65% to 90% reductions). The authors claim the combination of surface chemistry and  
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48 552 nano-topography explains such a result. The stability of the modified substrates was also evaluated  
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51 553 with contact angle measurements after 1 hour-treatment with 2.6% bleach, and no effect was  
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55 554 detected.  
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3 555           **2.3.2. Exogenous topography: micro/nanostructure through additive**  
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5 556           **strategies on polymers**  
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8 557 Polymer surface topography can also be modified by the deposition of a polymer of different  
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11 558 nature, but inorganic structures are also used as exogenous material to tune the topography.  
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16 559 Inspired by frog skin, this approach consisted in coating a PDMS layer with a block copolymer of  
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19 560 polystyrene (PS) and polylactic acid (PLA). Upon an hydrolytic treatment, the PLA blocks were  
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22 561 degraded generating microwrinkled surfaces due to the kinetic release of local strains along the  
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26 562 multilayer composite. In addition, the volumes freed from PLA blocks formed a nanoporous  
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29 563 structure with co-continuous nanochannels. Finally, a silicon oil was infused into the porous  
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32 564 structure thanks to capillary forces in order to produce a wrinkled SLIPS.<sup>62</sup> Antibiofouling  
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36 565 properties were assessed against the green algae species *Chlorella* sp. DT through cell coverage  
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39 566 analysis after immersion in a suspension in static conditions for 7 days. Further evaluation was  
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42 567 performed in fresh seawater for 7 days with blue-green algae species (*Arthrospira platensis* and  
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46 568 *Synechococcus lividus*), seawater algae species (*Isochrysis galbana*, *Tetraselmis ehui*) and  
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49 569 filamental cyanobacteria under different culture conditions that mimick the natural environments  
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52 570 of these microorganisms. Without the silicon oil (topographical approach only), in static condition  
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4 571 assays, antibiofouling performance was slightly improved when increasing wrinkle interspaces.  
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7 572 The author explains this tendency by indicating that the 15  $\mu\text{m}$  green algae has less attachment  
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10 573 points with increasing the wrinkle wavelength. However, performance dramatically improved after  
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13 574 silicon oil infusion, especially for the largest (75  $\mu\text{m}$ ) wrinkle wavelength. This illustrates the  
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17 575 beneficial effects of the combination of both topography and chemistry for antibiofouling  
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20 576 performance. Testing in dynamic conditions lead to similar results. The authors also tested an oil-  
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23 577 infused substrate without the wrinkling structure (chemical approach only). Its performance was  
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27 578 lower than substrates with combined approaches. However, it appeared that the lubricant is hard to  
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30 579 retain in dynamic conditions. Finally, optical transparency, anti-icing and self-cleaning properties  
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33 580 were demonstrated for the wrinkled oil infused substrates, confirming their high potential for  
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37 581 sensors or optical devices in marine industry.  
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41 582 Another example of topography modification with added material relied on the growth of Nickel  
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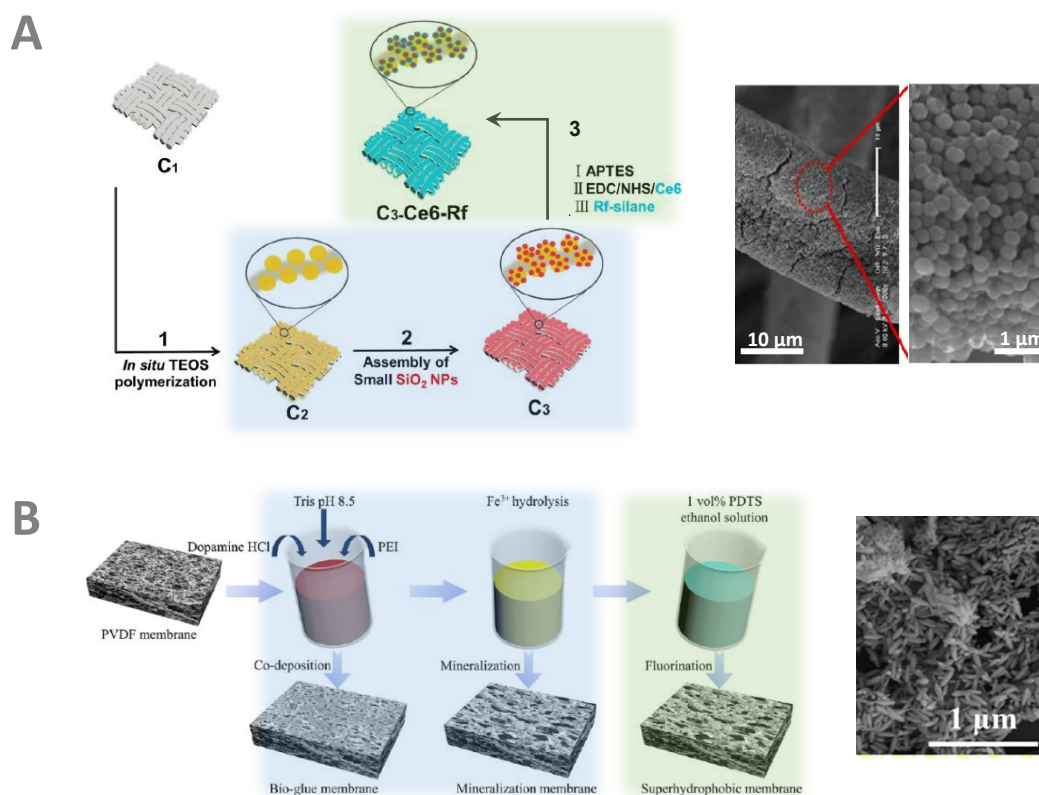
44 583 hydroxide  $\text{Ni}(\text{OH})_2$  onto a cotton fabric, followed by immersion in stearic acid solution and thermal  
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48 584 treatment to produce nickel stearate broccoli-like micro-structures. The modified cotton fabric was  
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51 585 turned superhydrophobic ( $160^\circ$ ), and suppressed bacterial growth of Gram-positive *S. aureus* and  
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55 586 Gram-negative *E. coli*, as well as fungal growth of *Candida albicans* even if the antibacterial  
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4 587 mechanism remains unclear ( $\text{Ni}^{2+}$  release is suggested to play a role).<sup>63</sup> Cotton fabric was also  
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7 588 modified with  $\text{SiO}_2$  nanoparticles enhanced with photodynamic activity of chlorin e6 (Ce6) and  
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10 589 functionalized with perfluoroalkyl-silane as described in Figure 9A. The textile's antibiofouling  
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13 590 property was evaluated against suspensions of Gram-positive *S. aureus* and Gram-negative *E. coli*.  
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17 591 Immersion and spraying in the dark were the two methods of exposure to the microorganisms,  
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20 592 modelling waterborne and airborne bacterial contamination, respectively. The synergistic effect of  
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23 593 superhydrophobic coating with perfluoroalkyl-silane and air trapping by hierarchical  
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27 594 nanostructures was proposed as an explanation for the significant reduction of bacterial adhesion  
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30 595 (*ca.* 90%) for both strains in the immersion approach. Similar results were obtained for the spraying  
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34 596 approach. Remaining bacteria elimination was expected to be eradicated by the photodynamic  
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37 597 activity of Ce6 that generates reactive oxygen species (ROS) upon visible light illumination. The  
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40 598 modified cotton textiles demonstrated a clear 100% killing rate against both *S. aureus* and *E. coli*  
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44 599 after 45 min of light illumination. Finally, modified textile fibers were exposed to whole blood and  
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47 600 managed to entirely repel the complex medium upon roll-off experiments.<sup>64</sup>  
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*Figure 9: Combined approach for exogenous topography design. A: cotton fabric enhanced with SiO<sub>2</sub> nanoparticles further coated with chlorin e6 and perfluoroalkylsilane (adapted with permission with reference <sup>64</sup>, Copyright 2019 American Chemical Society). B: PVDF membrane treated with β-FeOOH nanorods embedded in a polymer matrix, covered with a perfluorosilane (adapted with permission from reference <sup>65</sup>, Copyright Elsevier). Blue and green overlay indicate topography and chemistry modifications, respectively.*

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The final article of this sub-chapter deals with a polyvinylidene fluoride (PVDF) membrane modified through mussel-inspired strategy: the co-deposition of polydopamine and polyethylenimine as biogluce to embed β-FeOOH nanorods. A final top layer chemistry of perfluorosilane was also used to further improve the superhydrophobic properties (see Figure

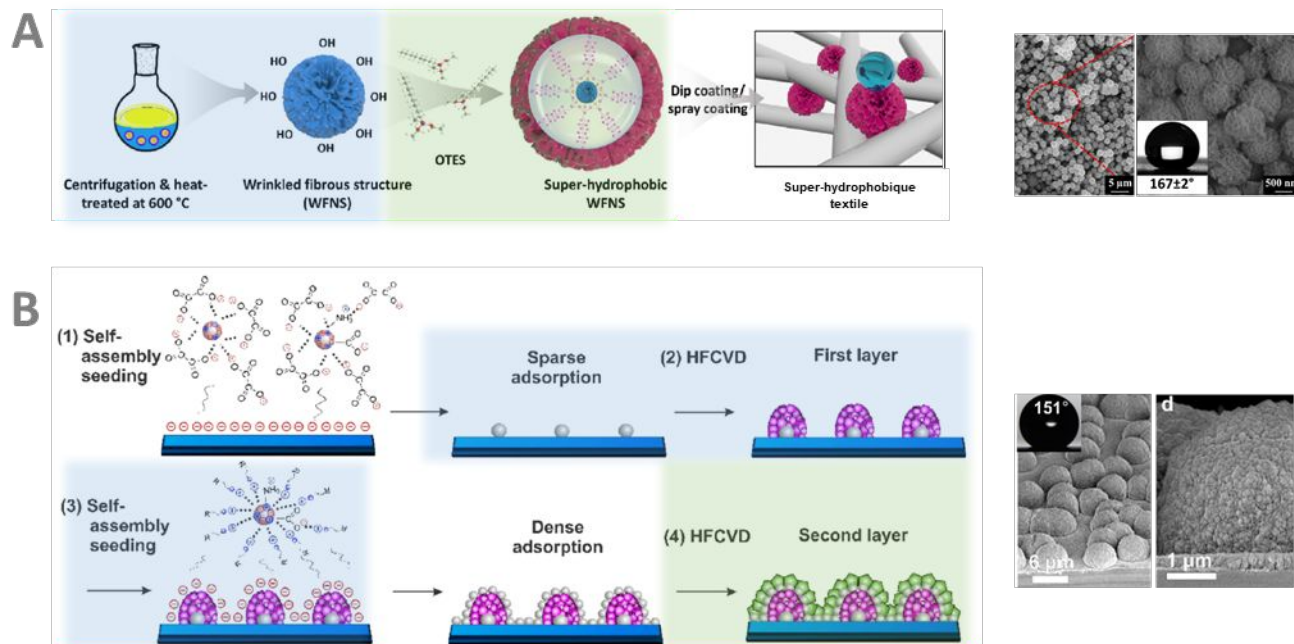
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3 613 9B).<sup>65</sup> Roll off angles below 6° were measured. Moreover, thermal and mechanical resistance were  
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7 614 evaluated for an hour against ultrasonic treatment, or 85°C aqueous medium. Contact angles were  
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10 615 not affected at all. The performance of direct contact membrane distillation (DCMD) was  
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13 616 performed with the pristine and enhanced membranes. Model wastewaters were used: a mixture of  
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17 617 NaCl, CaCl<sub>2</sub> and NaHCO<sub>3</sub> or NaCl and sodium dodecyl sulfate. The superhydrophobic membrane  
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20 618 outperformed the pristine membrane in every case with delayed compromised flux and no salt  
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23 619 crystallization. Even after 60h long DCMD testing, the nanorods were still present and the  
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27 620 membrane still functional. According to the author, the clear contribution of both the structured  
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30 621 nanorods and the chemical fluor layer contributed to reach the Cassie-Baxter regime that prevents  
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33 622 membrane wetting and explains such results.

#### 37 623 **2.4. Multi-substrate approaches**

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40 624 In this last subchapter the focus is given to the research articles that offer a combined topography  
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44 625 and chemistry approach for antibiofouling surface modification that have been successfully applied  
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47 626 to substrates of different nature. Indeed, from an applicative engineer perspective, such approaches  
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51 627 are of great interest since they might be used in various industrial fields, regardless of the nature of  
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4 628 the materials to be protected. These approaches inherently fall into the exogenous topography  
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7 629 category.  
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11 630 A robust superhydrophobic coating was developed through the use of wrinkled fibrous nano silica  
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14 631 functionalized with octyltriethoxysilane (OTES), as depicted in Figure 10A. Various substrates  
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17 632 (PVDF, glass, aluminium foil, fabric and paper) were treated with the wrinkled fibrous nano silica  
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21 633 dispersions by spray (hard substrates) or dip coating (soft substrates). The superhydrophobicity  
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24 634 was confirmed by contact angle measurements with daily liquid products such as honey, milk,  
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28 635 coffee, yogurt and juice. The robustness of the coating was demonstrated through abrasion testing,  
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31 636 finger wiping, tape adhesion and bending as well as before and after exposition to harsh  
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34 637 environmental conditions (UV light, organic solvents and salts, high temperatures). Also,  
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38 638 preliminary antifungal properties were revealed after exposition of a modified fabric to fungal  
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41 639 species under favorable conditions. The combination of the hydrophobic properties with the surface  
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44 640 roughness of the coral-reef like structure (and inherent air gaps) prevented the adhesion of micro-  
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48 641 organisms and drastically reduced the availability of nutrient in the liquid phase close to the  
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51 642 surface.<sup>66</sup>  
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644 *Figure 10: Multisubstrates combined chemical and topographical approaches. A: wrinkled nano silica*  
 645 *functionalized with octyltriethoxysilane deposited on textile, aluminium foil, glass, PVDF, fabric and*  
 646 *paper (adapted with permission from reference <sup>66</sup>, Copyright 2020 Elsevier). B: hot filament chemical*  
 647 *vapor deposition for micro and nano sized diamond hemispheres, covered with perfluorosilane (adapted*  
 648 *with permission from reference <sup>67</sup>, Copyright 2020 American Chemical Society). Blue and green overlay*  
 649 *indicate topography and chemistry modifications, respectively.*

650 Fang *et al* developed SLIPS with a one-step alcohol-assisted femtosecond laser irradiation that is  
 651 able to create porous micro/nanostructures on different substrates: stainless steel, nickel, glass and  
 652 polymer.<sup>68</sup> Fluoroalkylsilane modification was then carried out to reach superhydrophobic and  
 653 oleophilic surfaces. Indeed, this surface coating modified the WCA from 13° on porous stainless  
 654 steel, up to 143°. After silicon oil infusion onto the hydrophobic surface, the adhesion properties  
 655 were further modified, showing much lower adhesion to water droplets. This was demonstrated for

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4 656 various solutions with different components and viscosity: water, milk, ink, egg white, and  
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7 657 especially blood, which all simply slip down the tilted SLIPS. The substrates were tested in the  
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10 658 presence of green algae, a common fouling specie in marine applications. It was shown that the  
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13 659 combination of laser-irradiated structure and silicon oil lubricant was essential for obtaining a good  
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17 660 antibiofouling performance after seven days exposure to the green algae.

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21 661 An antibacterial, self-cleaning and antibiofouling coating was obtained on commercial titanium  
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24 662 alloys, silicon, quartz and ceramic substrates.<sup>67</sup> The bottom-up process based on hot filament  
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28 663 chemical vapor deposition (HFCVD) allowed for the modification of complex geometries and large  
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31 664 scale substrates. A pre-seeding of the substrates was performed with detonation nanodiamond,  
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34 665 followed by the HFCVD process that triggered the growth of diamond hemispheres. This procedure  
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38 666 was repeated one time to grow an additional, smaller, diamond structure onto the first one. Finally  
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41 667 the samples were chemically modified in liquid FDTs after an oxygen plasma treatment (see Figure  
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44 668 10B). Antibacterial activity was evaluated against *P. aeruginosa* (MCCC1A00099) and *E. coli*  
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48 669 (ATCC 25922) by using live/dead™ staining after 24 hours incubation. These tests confirmed the  
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51 670 crucial role of the structured diamond film with *ca.* 90% and 99% reduction in bacterial adhesion  
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55 671 compared to untreated substrates for *P. aeruginosa* and *E. coli*, respectively. In addition, two



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4 672 biofouling tests with marine contaminants *C. vulgaris* (FACHB 44) and *Ulothrix speciosa* (FACHB  
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7 673 494) were conducted. Again, the structured and fluorinated samples demonstrated the best  
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10 674 antibiofouling results compared to untreated samples, but also compared to the samples modified  
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13 675 with either topography or chemistry alone. Thus it is the synergistic effect of topography and  
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17 676 surface chemistry that allows for such antibiofouling effect.

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21 677 As a conclusion, in a vast majority, the combined topography and chemistry hydrophobic  
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24 678 approaches to produce antibiofouling surfaces lead to superhydrophobic wettability, often  
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28 679 achieving Cassie-Baxter regime. In most articles, this result is obtained only by combining  
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31 680 topography with a specific surface chemistry. The antibiofouling property thus arises from the  
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34 681 prevention adhesion mechanism cited in Figure 1. However, despite the various topography  
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38 682 designing techniques, the hydrophobic chemical entities employed are limited to either fluorine-  
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41 683 based polymers or silanes, alkyl chains or infused silicon or fluorine-based oils. The next chapter  
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44 684 will demonstrate how wide the hydrophilic chemical entities library is for antibiofouling surface  
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48 685 development with combined topography and chemistry approaches.

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52 686 **3. Combined topography and hydrophilicity for multiple antibiofouling**  
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55 687 **mechanisms**  
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4 688 As explained in the introduction, superhydrophilic surfaces can also be used for antibiofouling  
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7 689 surface development. In this chapter we will focus on research articles where superwettability has  
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10 690 been achieved by combining topography and chemistry with the aim to repel biomolecules and  
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13 691 microorganisms. Many different techniques have been used to develop the functional topography  
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17 692 and deposit the chemistry of interest. All the approaches described in this chapter are detailed in  
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20 693 Table S3 of the Supporting information.

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24 694 Superhydrophilic surfaces have been less explored for antibiofouling applications than  
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28 695 superhydrophobic one. This can explain why less common ground can be found in the literature  
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31 696 and why there is such a variety of solutions. In addition, as it can be seen in Figure 2, there is a  
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34 697 wide range of chemical approaches leading to hydrophilic antibiofouling surfaces. This can make  
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38 698 it challenging to find links between the various articles. However, as in the previous chapter  
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41 699 concerning hydrophobic approaches, three types of substrates have been studied: metals, glass and  
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45 700 polymers. This will be used to structure this part of the review, thus creating three sub-chapters.

### 48 701 **3.1. Metallic substrates**

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4 702 Metallic substrates are not a common material used for hydrophilic-based approaches, oppositely  
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7 703 to hydrophobic strategies. However, these surfaces show very different characteristics,  
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10 704 demonstrating the diversity of hydrophilic strategies for antibiofouling studies on metals.

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14 705 The first example of such surfaces are TiO<sub>2</sub> nanotubes coated with a Poly(ethylene) glycol (PEG)-  
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17 706 silane, which showed different activities against fibrinogen and *S. aureus* depending on the size of  
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21 707 the nanotubes. For this study, An and co-workers used potentiostatic anodization of Titanium to  
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24 708 create the nanotubular effect. Two dimensions were created: nanotubes of 20 and 80 nm diameter  
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28 709 (TN20 and TN80 respectively). This was followed by a reaction with a PEG-silane solution  
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31 710 allowing the nanotubes to achieve better hydrophilicity (see Figure 11B). Although TN80 was more  
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34 711 hydrophilic with a WCA of 19°, TN20 was the only surface which showed both low adhesion of  
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38 712 model foulant fibrinogen and low friction coefficient. *S. aureus* was used to test the bacterial  
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41 713 adhesion. Surprisingly, PEG-coated TN20 showed a high adhesion, similar to Ti and PEG-coated  
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44 714 Ti, whereas all the other substrates, including PEG-coated TN80, repelled the bacteria. It seems  
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48 715 that, depending on the size of the nanotubes, and therefore, on the available surface contact area,  
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51 716 the antibiofouling effect can be inhibited.<sup>69</sup>

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4 717 This has also been shown through the study of marine diatoms on zwitterion-coated structured  
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7 718 stainless steel substrates. Here, unlike the previous study where the topography of the initial  
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10 719 substrate was modified, an exogenous material was added to create the topography. Indeed, the  
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13 720 initial substrates were coated with aluminium through flame spray technique and micropatterned  
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17 721 with a shielding steel mesh. A layer of PDMS was then formed on the samples and allowed for  
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20 722 subsequent chemical functionalization with the zwitterionic molecule [2-(Methacryloyloxy)ethyl]-  
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23 723 dimethyl-(3-sulfopropyl)-ammonium hydroxide (pSB) through 3,4-dihydroxyphenylalanine  
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27 724 (DOPA) binding. Bovine Calf Serum proteins were used to simulate the conditioning layer  
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30 725 formation on the substrates. An antibiofouling activity was observed but was fully attributed to the  
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33 726 hydration layer brought by the pSB and the electrostatic interaction between bovine proteins and  
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37 727 dipole moment of the sulfobetaine groups. No influence of the topography was detected. The  
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40 728 antimicrobial effect of the substrates was studied with marine diatoms *Cylindrotheca closterium*  
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44 729 which were incubated with the samples presenting both chemical and topographical modifications,  
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47 730 in an artificial seawater-based medium. Confocal laser scanning microscopy showed no adhesion  
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50 731 to the protuberances. However, pSB modification of reference flat samples resulted in a lower  
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54 732 density of diatoms. It is thought that the increase of the specific surface area of the patterned  
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4 733 substrates is responsible for the higher adhesion of diatoms. A hypothesis that can be raised is that  
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7 734 the protuberances are too big in comparison to the size of the tested micro-organisms.<sup>70</sup>  
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11 735 One last type of metallic surface that has shown promise in antibiofouling applications due to its  
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14 736 hydrophilicity is bioinspired self-cleaning mucus-like hierarchical ciliary bionic antifouling  
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18 737 surfaces (SMCAS). These complex surfaces made of polyamide microfibers covered with carbon  
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21 738 nanotubes (CNT) and poly(vinyl alcohol) (PVA) hydrogel particles, that mimic the skin of marine  
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24 739 species, were designed by Ren *et al* with electrostatic flocking technology and solution spray (see  
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28 740 Figure 11A) to impart the so-called camouflage effect to steel surfaces, making them hard to be  
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31 741 recognised by the various foulants. Marine bacteria *Marinobacter lipolyticus* SM19(T) and  
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34 742 microalgae *Nitzschia closterium f. minutissima* were used to evaluate anti-adhesion performance of  
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38 743 the SMCAS surface. After 24 hours of co-culture, SMCAS integrally suppressed the bacterial  
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41 744 adhesion, showing better results than model PVA/CNT hydrogel which reduced the bacterial  
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45 745 adhesion to  $2.0 \times 10^3$  cells/cm against  $5.6 \times 10^5$  cells/cm on silicon. The efficacy of SMCAS,  
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48 746 explained by enhanced water-retaining, was also shown upon microalgae contact for as long as 3  
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51 747 weeks. Concomitantly, microfibers swaying along with the flow of seawater contributed to remove  
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55 748 the adhered contaminants.<sup>71</sup>  
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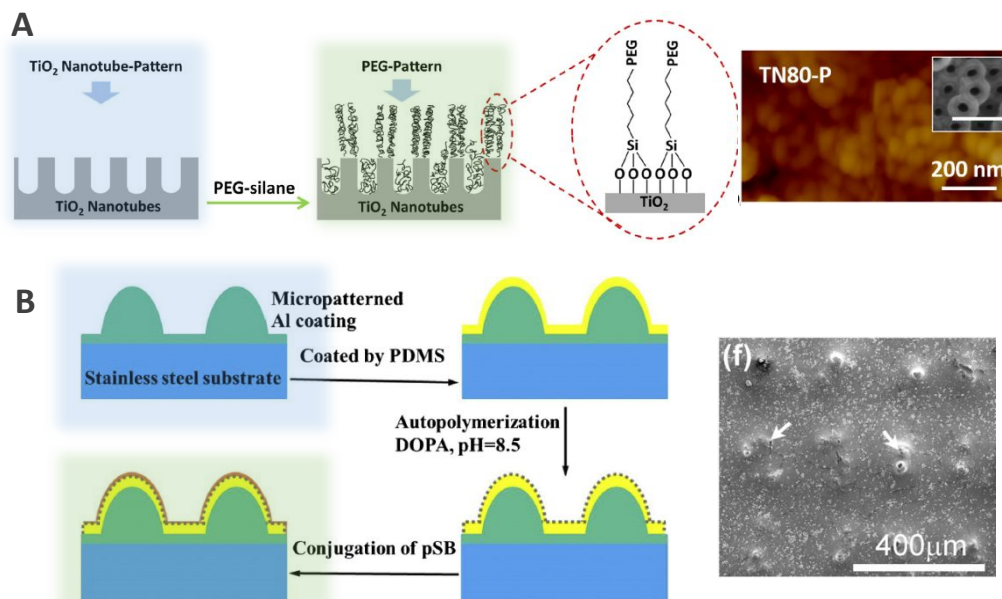


Figure 11: Antibiofouling strategies combining hydrophilic polymers and topography on metallic substrates. A: PEG silane on nanotubes (adapted with permission from reference <sup>69</sup>, Copyright 2019 Elsevier). B: Micropatterned Al coatings with zwitterion surface modification (adapted with permission from reference <sup>70</sup>, Copyright 2016 Elsevier). Blue and green overlay indicate topography and chemistry modifications, respectively.

### 3.2. Glass substrates

In this chapter, modified glass substrates with a hydrophilic antibiofouling activity will be described. The first three articles concern surfaces where endogenous topography has been created. The following articles use an exogenous material to tune the topography. They also show surface chemistry with a bactericidal effect on tested microorganisms, on top of the anti-adhesive effect caused by the hydrophilic coating on topography. This has enabled the creation of surfaces which

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4 762 can kill bacteria as well as impede their adhesion. The following articles use an exogenous material  
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7 763 to tune the topography.  
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11 764 For example, nisin is an antimicrobial peptide with a hydrophilic end that has been combined to  
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14 765 microstructured glass to create efficient substrates against bacteria and diatoms. This study was  
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18 766 carried out by Lou and co-workers who began by structuring glass through ion etching before  
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21 767 functionalizing with nisin. This peptide binding protocol led to strong coatings which were stable  
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24 768 in sterile artificial sea water even after 10 days. The antibiofouling activity was assessed against  
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28 769 bacteria *Bacillus sp.* and diatoms *P. tricornutum*. The quadrangle-shaped microstructure alone  
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31 770 promoted bacterial fouling as the interspaces were bigger than the cells. However, with the nisin  
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34 771 immobilization, antibacterial effect was confirmed. Nevertheless, the synergistic effect of  
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38 772 microstructure and surface chemistry appeared hard to find for bacterial fouling. Against diatoms,  
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41 773 on the other hand, which are bigger than bacteria (10  $\mu\text{m}$  vs 1-2  $\mu\text{m}$ ), the anti-adhesion effect of  
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44 774 the microstructure alone was stronger. With the nisin peptide treatment, an even better anti-  
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48 775 adhesion effect was detected, proving the synergistic effect of the combined approach against algal  
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51 776 foulants. Also, it was shown that an increased depth of the microstructure enhanced the anti-  
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54 777 adhesion effect of both untreated and nisin-treated glass microstructures against the diatoms.<sup>72</sup>  
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4 778 Polyacrylic acid (PAA) has also been used for its antibacterial effect. However, it has been shown  
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7 779 to have a gram-dependant efficiency. In a study by Chen *et al*, layer-by-layer deposition of  
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10 780 polyelectrolytes polyvinylamine (PVAm) and PAA was the chosen method for obtaining a  
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13 781 functional coating and femto-second laser pulsing was used to acquire micro and nano-patterned  
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17 782 borosilicate glass (see Figure 12B). When testing with *E. coli* K-12 and *S. aureus* 208, it was  
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20 783 confirmed that the positive charge surface enhanced bacterial collection. *E. coli* adhesion increased  
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23 784 faster than *S. aureus* owing to its higher outer-membrane charge. Live/Dead™ staining after a 4 h  
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27 785 incubation confirmed the bactericidal activity. It was suggested that the nanostructures contributed  
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30 786 more to the bactericidal effect than the microstructures. However, no damage was observed on  
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33 787 mammalian cells.<sup>73</sup>

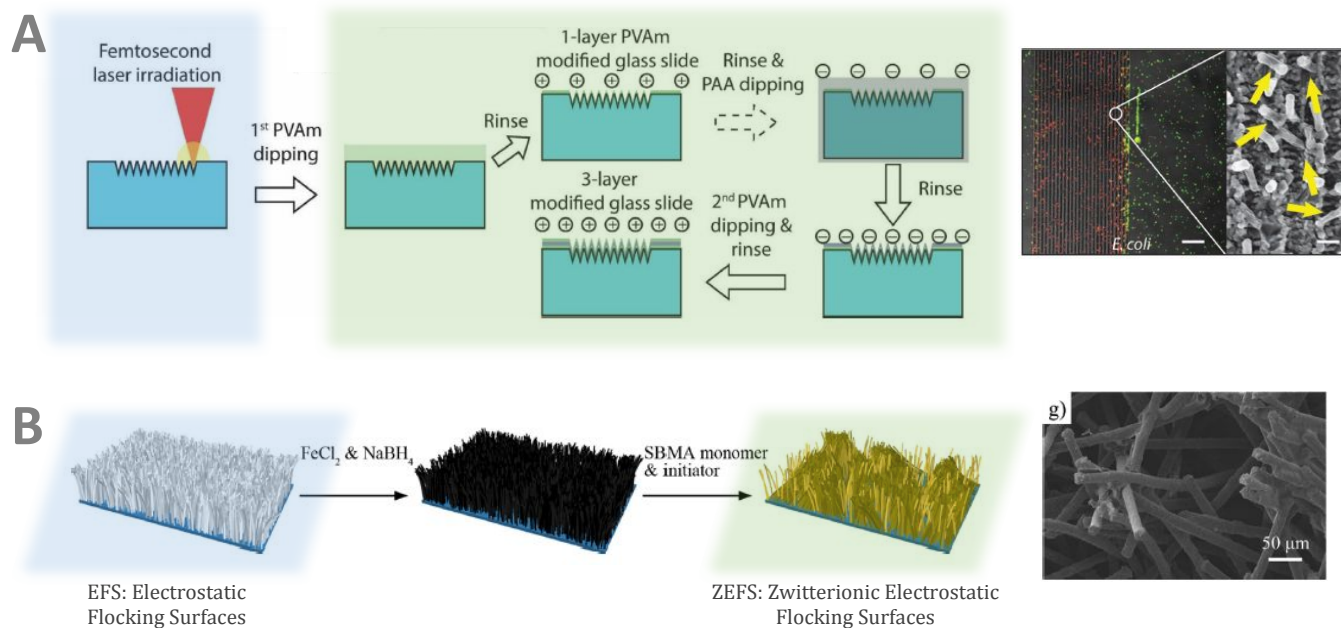
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37 788 The same difference of adhesion depending on the type of bacteria was demonstrated with a film  
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40 789 of poly-(acrylic acid-co-(poly(ethylene glycol)diacrylate)) (poly(AAC-co-PEGDA)). Here, the  
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44 790 hydrogel was spin-coated onto functionalized cover slips and then treated with an argon plasma to  
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47 791 develop micro-sized wrinkles. The acrylic acid was efficiently bactericidal against both *S. aureus*  
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50 792 and *E. coli*, and the wrinkles contributed to lowering the amount of live microorganisms. However  
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53 793 the engineered surfaces were slightly more efficient on Gram-positive *S. aureus*.<sup>74</sup>



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4 794 Liu and co-workers produced a superhydrophilic layer of Poly(sulfobetaine methacrylate)  
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7 795 (PSBMA) by sub-surface initiated atomic transfer radical polymerization (SSI-ATRP) onto a glass  
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10 796 substrate. This technique allowed for the *simultaneous* tuning of both *topography and chemistry*  
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13 797 (as described in Figure 2). Micro-sized wrinkles were obtained, with size parameters depending on  
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17 798 the reaction time. A first study reveals the performance of the PSBMA structured surface against  
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20 799 marine environment conditions<sup>75</sup>. Static antibiofouling was assessed with red algae *Porphyridium*  
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23 800 *sp.* and diatoms *Navicula sp.* for several hours. The resulting micro-organism densities were  
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27 801 reduced by two orders of magnitude for SSI-ATRP produced surfaces compared to blank surfaces.  
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30 802 Furthermore, on structured surfaces resulting densities were 4 to 6 times smaller than on  
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33 803 unstructured ones, indicating the beneficial synergistic effect of superhydrophilic surface chemistry  
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37 804 and microsized topography. Ocean field assays over 45 days were performed. According to the  
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40 805 author, the engineered surfaces better resisted the biofouling even if the available pictures seem  
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44 806 complicated to compare. The SSI-ATRP also improved the long-term stability of the polymer  
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47 807 layer.<sup>75</sup>  
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51 808 The same team used the SSI-ATRP produced PSBMA layer in another study where the adhesion  
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54 809 of different types of foulants was investigated: macromolecules (BSA, lysozyme and fibrinogen),  
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4 810 bacteria (*E. coli* and *B. subtilis*) and diatoms (*Chaetoceros calcitrans*).<sup>76</sup> Here, a walnut-shell-like  
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7 811 microsized surface topography was obtained. It was shown that a 2  $\mu\text{m}$  PSBMA layer prevents  
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10 812 macromolecular fouling, while a 5-10  $\mu\text{m}$  thickness is more efficient against bacteria and diatoms.  
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13 813 After a longer reaction time (8 h instead of 1, 2 or 4), the regular walnut-shell-like structures  
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17 814 became irregular blocks and antibiofouling properties were lost.<sup>76</sup>  
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21 815 PSBMA was also chosen to create zwitterionic electrostatic flocking surfaces (ZEFS). Unlike the  
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24 816 two formerly mentioned articles, here the topographical and chemical modifications were reached  
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28 817 through separate steps. The topography was first obtained by depositing nylon fibers onto glass  
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31 818 substrates by electrostatic flocking. A thin film of PSBMA was then wrapped around the  
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34 819 microfibers by radical polymerization catalyzed by Fe (see Figure 12A). It was demonstrated that  
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38 820 the diatoms *N. closterium f. minutissima* adhered very little to the fibers due to the low contact area  
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41 821 caused by their morphology. Further tests were carried out using common mussel species *Mytilus*  
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45 822 *edulis*, capable of choosing where to attach to the surface through exploration and thread secretion.  
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48 823 On a test board composed of glass, PDMS and ZEFS, the mussels avoided the zwitterionic coated  
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51 824 fibers, and preferentially stuck to glass.<sup>77</sup>  
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826 *Figure 12: Fighting biofouling with hydrophilic coatings and topography on glass substrates. A: Layer-by-*  
 827 *layer deposition of polyelectrolytes PVAm and PAA on nanopatterned borosilicate glass (adapted with*  
 828 *permission from reference <sup>73</sup>, Copyright 2020 Elsevier). B: zwitterionic electrostatic flocculation surface*  
 829 *produced with PSBMA (adapted with permission from reference <sup>77</sup>, Copyright 2021 Elsevier). Blue and*  
 830 *green overlay indicate topography and chemistry modifications, respectively.*

### 831 3.3. Polymer substrates

832 Polymer substrates are the most represented in the chapter focusing on hydrophilic combined  
 833 approaches. In nearly two thirds of the research articles in this chapter, the initial material is a  
 834 polymer. However, as well as the wide diversity found in the production of topography and the  
 835 surface chemistry, there is also a large range of polymers themselves. These different polymers can  
 836 have different physico-chemical properties and are therefore not all suited for the same  
 837 applications. To facilitate reading, in this subchapter, the articles have not been organized

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4 838 depending on the polymers, but rather on the application they were chosen for: marine industry,  
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7 839 water filtration, medical devices.  
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#### 10 840 **3.3.1.1. Marine industry**

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12 841 In this paragraph, the articles all aim to develop strategies for the marine industry where biofouling  
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16 842 can have a significant economic impact. Some teams use biomimetic materials, as sea species have  
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19 843 developed complex skin, shell or leaf surfaces to repel other, smaller organisms. Interestingly, they  
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23 844 all use PDMS as the initial substrate which is directly modified to obtain the desired topography.  
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27 845 In the first article, PDMS films were stretched and plasma-treated to obtain a wrinkled surface.  
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30 846 Silanization was then performed followed by surface-initiated atom transfer radical polymerization  
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33  
34 847 (SI-ATRP) to produce poly(ethylene glycol)methacrylate (POEGMA) or poly(3-sulfopropyl-  
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37 848 methacrylate) potassium salt (PSPMA) brushes on the structured surface. The growth of the  
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40 849 polymer brushes did not have an impact on the structure. *Ulva* zoospores and microalgae *Chlorella*  
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44 850 were mixed in the same batch at different concentrations to evaluate the marine antibiofouling of  
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47 851 the different samples. In static conditions over 7 days, the PDMS wrinkled surface was able to  
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50 852 reduce the amount of adhered *Chlorella* more than *Ulva* since the zoospores are smaller than the  
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54 853 wrinkled surface size. The POEGMA and PSPMA layers on flat PDMS also showed reduced cell  
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4 854 densities. The combination of wrinkles and polymer brushes led to the smallest cell densities.  
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7 855 PSPMA-modified PDMS (both smooth and wrinkled) was more efficient than the surface modified  
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10 856 with POEGMA brushes against *Ulva* zoospores. However, there was no significant differences  
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13 857 between the two polymers against *Chlorella*. In dynamic conditions, very little biofouling from  
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17 858 *Chlorella* was detected: from ~240 cells/mm<sup>2</sup> on PDMS to under 20 cells/mm<sup>2</sup> on the modified  
18  
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20 859 substrates. Finally, a sea water assay was performed for 2 months and clearly showed the superior  
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24 860 antibiofouling effect of SI-ATRP-modified wrinkled PDMS compared to wrinkled-only or bare  
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27 861 PDMS. Again, both polymer brushes showed similar antibiofouling effects.<sup>78</sup>  
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31 862 Brzowska's team took inspiration from marine decapod crab *Myomenippe hardwickii* and  
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34 863 replicated its surface composed of big and small features allowing it to repel species of various  
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38 864 sizes. To enhance the antibiofouling effect, the biomimicking structure was combined with surface  
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41 865 chemistry. Two strategies were carried out: modification with zwitterionic sulfobetaine polymer  
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45 866 brushes and layer-by-layer coating of poly(isobutylene-alt-maleic anhydride) and  
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48 867 polyethyleneimine (PEI) (Figure 13A). Tests were carried out with cyprids *Amphibalanus*  
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51 868 *amphitrite* and diatoms *Amphora coffeaeformis*. For both species, the lowest adhesion was  
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55 869 achieved with zwitterion brushes on patterned surfaces. This article also highlights the difference  
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4 870 between *in vitro* antibiofouling experiments and tests carried out in the field where hydrodynamics  
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7 871 have a non-negligible effect.<sup>79</sup>  
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10  
11 872 A similar approach consisted of mimicking the topography of algae *Laminaria japonica* by molding  
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14 873 PDMS. Layer-by-layer coatings were also applied. In this case, they were composed of sodium  
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18 874 alginate and (guanidine-hexamethylenediamine-Polyethyleneimine) (poly(GHPEI)) (Figure 13B).  
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21 875 Structuring and surface chemistry modification both led to better hydrophilicity in comparison to  
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24 876 bare PDMS. The most hydrophilic, with a WCA of 35°, was the (GHPEI-ALG)-coated structured  
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28 877 substrate. The prepared samples were tested against diatoms *N. closterium* and *P. tricornutum*.  
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31 878 Structured surfaces repelled diatoms better than smooth ones. However, the combination of  
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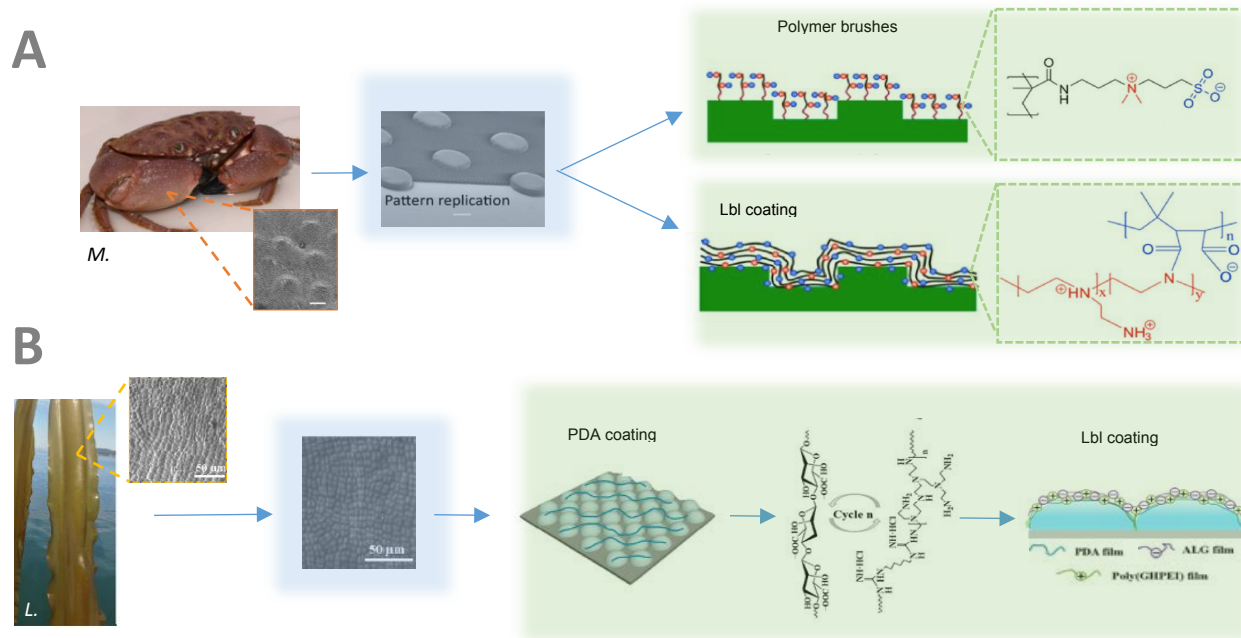
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34 879 topography and chemistry gave the most effective surfaces, with a decrease in diatom density from  
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38 880 nearly 1200 diatoms/mm<sup>2</sup> on smooth PDMS to under 10 diatoms/mm<sup>2</sup> on the complex surface.  
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41 881 Over a period of 14 days, the developed material also inhibited diatom growth contrarily to other  
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44 882 materials. Antibacterial activity was also studied with *E. coli* and was evaluated to be roughly  
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48 883 96%.<sup>80</sup>  
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885 *Figure 13: Bioinspired combinations of chemistry and topography on PDMS to fight marine biofouling. A:*  
 886 *Biomimicking marine decapod crab *M. hardwickii* structure and modifying through polymer brushes or*  
 887 *layer-by-layer coating (adapted with permission from reference <sup>79</sup>, Copyright 2014 American Chemical*  
 888 *Society). B: Layer-by-layer coatings on molded PDMS inspired by algae *L. japonica* (adapted with*  
 889 *permission from reference <sup>80</sup>, Copyright 2020 Elsevier). Blue and green overlay indicate topography and*  
 890 *chemistry modifications, respectively.*

### 891 3.3.1.2. Water filtration

892 We have seen so far many different applications of antibiofouling surfaces but one important  
 893 industry remains to be looked at: water filtration. Indeed, to avoid contamination of drinking water,  
 894 it is vital that the polymer membranes that are used resist the formation of biofilm. Hydrophilic  
 895 coatings have a true importance in this field to enhance the water separation. This is what will be  
 896 studied in the next paragraph which is organised by type of polymer membrane used as the initial  
 897 substrate.

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4 898 The first one we will concentrate on is the polyamide (PA) membrane which has been chemically  
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7 899 and topographically modified by various teams, leading to efficient materials for water treatment  
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10 900 without biofilm formation.

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14 901 Weinman and Husson for instance, structured PA membranes with nano lines and grooves by  
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17 902 thermal embossing, and coated them with poly(ethyleneglycol) diglycidyl ether (PEGDE) ( Figure  
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21 903 14A). In comparison to pristine membranes, for which the flux was reduced by over 20% over a  
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24 904 period of 2 h, the patterned membranes did not have such a negative effect on the desired  
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28 905 application, with a maximum reduction of 8%. The PEGDE coating caused a slight flux reduction  
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31 906 on the patterned membranes but this impact did not increase with its concentration (5 or 15 wt%).

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34 907 In all experiments the salt rejection remained close to the 95% specified by the manufacturer. To  
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38 908 test the antibiofouling capacity of these membranes, sodium alginate was used as a model foulant.

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41 909 It was demonstrated, by quantifying the flux over time, that both the patterning and the chemical  
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45 910 coating decreased the fouling on the membranes. The combination of both surface hydrophilicity  
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48 911 and improved hydrodynamics induced by the lines and grooves, gave the best results.<sup>81</sup>

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52 912 Choi's team, who had previously studied antibiofouling techniques based on cylindrical TiO<sub>2</sub>  
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55 913 pillars on PA membranes,<sup>82</sup> further improved their technique by upgrading the structuration of the  
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4 914 membranes to shark skin inspired topography, namely Sharklet™. They reached thin film composite  
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7 915 microstructured membranes using a series of steps including phase separation micromolding and  
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10 916 layered interfacial polymerization.<sup>83–85</sup> The structure was then combined with coating of  
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13 917 hydrophilic tannic acid, deposited from the liquid-phase, giving the membrane an anti-adhesif  
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17 918 effect (Figure 14B).<sup>85</sup> Study of the modified membranes revealed NaCl rejection and permeability  
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20 919 towards water were very similar between uncoated and coated membranes. In fact, the water  
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24 920 permeance was slightly improved due to the hydrophilicity of the coatings. As with the nanopillar  
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27 921 arrays from their previous study,<sup>82</sup> the sharkskin nanostructure coupled with a chemical coating of  
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30 922 tannic acid led to a decrease in *P. aeruginosa* attachment, shown qualitatively by live/dead™  
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34 923 imaging. In dynamic conditions, an isolated vortex is created by the Sharkskin protrusions,  
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37 924 decreasing furthermore the ability of *P. aeruginosa* to adhere to any surface<sup>84</sup>. In their publication  
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40 925 from January 2022, Zhao *et al.* also used tannic acid on nanofiltration membranes for its  
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44 926 antibiofouling effect. They deposited it on a polyacrylonitrile membrane modified with  
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47 927 Glutaraldehyde (GA)-crosslinked PEI-SBMA to give it a microstructure which was tuned by  
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50 928 varying the concentrations of GA.<sup>86</sup>  
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4 929 Another material with physico-chemical properties that allow the fabrication of membranes is  
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7 930 polysulfone (PSF). Various types of PSF membranes exist and have raised interest in the scientific  
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10 931 community.

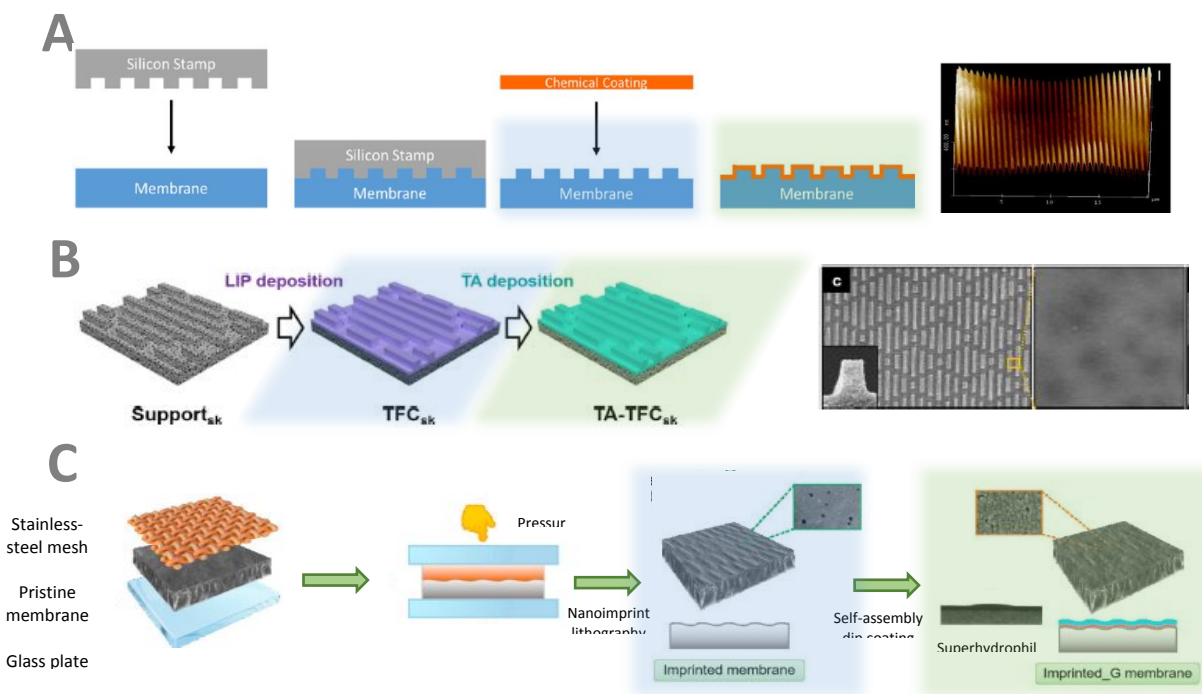
11  
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13 932 In a first study, a Polyethersulfone (PES) membrane was coated with a mixture of cellulose  
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17 933 nanofibrils (CNF) and PVA. This treatment imparted PES membranes with both nano-textured  
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20 934 roughness and charged surface chemistry. PVA was added to crosslink the film and improve its  
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24 935 adhesion to the substrate, decreasing the average roughness from around 30  $\mu\text{m}$  to 10  $\mu\text{m}$ .

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27 936 According to the author, a smaller specific surface area is expected to better prevent molecule  
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30 937 adhesion. On the contrary of the wettability, which did not change, conserving the membrane's  
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34 938 efficiency; the surface charge was impacted by the coating:  $\zeta$ -potential was reduced from -20 mV  
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37 939 to -40 mV around the plateau at pH 5, indicating a higher amount of negatively charged hydroxyl

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40 940 and aldehyde groups. BSA adsorption on the coated membrane was evaluated using quartz crystal  
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44 941 microbalance with dissipation monitoring (QCM-D) and was shown to be very limited. It is  
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47 942 believed that the abundant hydrophilic groups of PVA/CNF layer suppress the interactions with  
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50 943 the protein. A biofilm study with *E. coli* revealed that the bacterial coverage was also almost  
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54 944 eliminated. In this case, the promising results can be explained by the combination of both surface

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4 945 chemistry, which promotes electrostatic repulsion of bacteria and a bactericidal effect, and tuned  
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7 946 surface roughness, which reduces the specific surface area.<sup>87</sup>  
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10 947 Lin and his team also chose to begin with PSF membranes, modifying them with a combination of  
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13 948 tannic acid (TA), PEI and (3-amino-1-propanesulfonic acid), otherwise known as taurine. Indeed,  
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17 949 these three molecules were co-deposited at the surface of the membrane, before interfacial  
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20 950 polymerization with trimesoyl-chloride. Turing striped structures were formed with 0.2% taurine  
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24 951 content during the interfacial polymerisation. Humic acid, sodium alginate and BSA were chosen  
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27 952 as model foulants. Flux recovery ratio was close to 98% against humic acid confirming excellent  
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30 953 antibiofouling effect. Sodium alginate and BSA tests gave slightly lower antibiofouling  
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34 954 performance (with a flux recovery ratio of 90% and 93% respectively), partly explained by higher  
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37 955 molecular weights. Here again, it is the combination of both chemistry and topography that led to  
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40 956 the best designed ultrafiltration membrane: the strong hydration layer arising from the zwitterionic  
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44 957 nature of taurine prevented the adsorption of model organic foulants, and meanwhile, the  
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47 958 hydrophilic striped surface allowed for a mild enhancement of water flux as a consequence of  
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50 959 increased specific surface area.<sup>88</sup> In a similar study from the same research team, interfacial  
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54 960 polymerization was combined to a sol-gel reaction in order to explore a new approach to limit

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4 961 biofouling.<sup>89</sup> This led to controlled pore size and an increase in water permeability and selectivity  
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7 962 of the membrane. The surface was also enriched with hydroxyls that increased the hydrophilicity  
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10 963 and decreased the biofouling of BSA.  
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13 964 Finally, the last type of membrane that was found to be relevant for this review is the PVDF  
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17 965 membrane.  
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967 *Figure 14: Combining topography and hydrophilic coatings to combat biofouling on polymeric*  
 968 *membranes for water treatment. A: Structured Polyamide (PA) membrane coated with*  
 969 *Poly(ethyleneglycol)diglycidylether (PEGDE) (adapted with permission from reference <sup>81</sup>, Copyright 2016*  
 970 *Elsevier). B: PA membrane modified with Sharklet™ topography and coated with tannic acid (adapted*  
 971 *with permission from reference <sup>85</sup>, Copyright 2021 Elsevier). C: Nanoimprint lithography and self-*  
 972 *assembly dip-coating to modify PVDF membranes (adapted with permission from reference <sup>90</sup>, Copyright*  
 973 *Elsevier 2020). Blue and green overlay indicate topography and chemistry modifications, respectively.*

974 For example, microporous PVDF membranes have been coated with poly(N-vinyl-pyrrolidone)  
 975 (PVP) by initiated Chemical Vapor Deposition (iCVD). In this case, to increase the adhesion of the  
 976 hydrophilic PVP onto the membrane, a prime layer of crosslinking agent poly (ethylene glycol  
 977 diacrylate) (PEGDA) was deposited before coating with copolymer poly(VP-co-EGDA). Different  
 978 ratios of crosslinking were tested and the effect on FTIR and WCA were analysed. The latter  
 979 reached nearly 0°, as the water droplets got absorbed by the membrane in less than 3 s. It is thought

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4 980 that this superwettability is only achieved by combining the two factors: the hydrophilicity of the  
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7 981 PVP coatings on the one hand, and on the other hand, the porous structure that allows the water  
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10 982 droplets to spread rapidly throughout the membrane. Antibiofouling was tested using model protein  
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13 983 BSA and fluorescently stained *E. coli*. The amount of BSA was reduced from 36  $\mu\text{g}/\text{cm}^2$  to under  
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17 984 2.2  $\mu\text{g}/\text{cm}^2$  upon coating the PVDF membrane. This quantity was slightly increased after durability  
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20 985 tests but still remained 90% lower than adsorption on pristine membranes. However, for these  
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24 986 estimations, only the apparent surface area was studied. It is thought that the internal pores have a  
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27 987 large surface area, thus decreasing furthermore the actual protein adsorption.<sup>91</sup>  
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30 988 Furthermore, in an article by Ma and co-workers, the PVDF substrates were enhanced by  
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34 989 modification of topography and grafting of nanoparticles decorated with hydrophilic chemical  
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37 990 functions. A micro scale surface pattern was formed through imprinting with a stainless steel mesh.  
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40 991 Further nano scale topography was achieved by adding an exogenous material. Indeed, the  
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44 992 imprinted membrane was dipped into a suspension of amine-terminated  $\text{SiO}_2$  nanoparticles (see  
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47 993 Figure 14C). Simultaneously, amine functions that are not involved in the surface binding thus  
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50 994 represent the new surface chemistry of the membrane. It was noted that nanoparticle  
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54 995 functionalisation alone lead to high roughness, which was wiped out when combined with micro-

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3 996 scale imprinting. Full wetting of water droplets observed during contact angle measurements  
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7 997 demonstrated the superhydrophilic nature of the modified membrane. Antibiofouling properties  
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10 998 were evaluated in both static conditions against bacteria suspensions (*Bacillus thuringiensis* and *E.*  
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13 999 *coli*) at  $10^8$  CFU/mL, and in dynamic conditions upon filtration tests with a practical mixed liquor  
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17 1000 sample in a full-scale aerobic membrane bioreactor. SEM analysis was used to detect the presence  
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20 1001 of bacteria. Fewer seemed to be detected on the modified membrane after rinsing, although no  
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23 1002 quantitative analysis was carried out. For the filtration tests, flux recovery measurements were  
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27 1003 performed to quantify the antibiofouling performance against the mixed liquor. The modified  
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30 1004 membrane offered a 45% higher flux recovery compared to pristine membranes, which is explained  
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33 1005 by the hydration layer arising from the superhydrophilicity, and the wave-like micro-structure that  
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37 1006 promotes turbulent flow, both reducing the adhesion of foulants to the membrane.<sup>90</sup>  
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### 40 1007 **3.3.1.3. Medical devices**

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43 1008 Polymers are also often used in the medical field as they have many advantages in comparison to  
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47 1009 other materials. In the case of medical devices, developing strategies to stop biofilm formation on  
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50 1010 the polymeric surface is even more critical as it can often lead to nosocomial infections.  
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4 1011 In this study, Park *et al* used a cellulose acetate (CA) solution which was drop-cast on a PDMS  
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7 1012 master mold resulting in a flexible CA nanoneedle array. After plasma treatment, an aqueous  
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10 1013 solution of 2-methacryloyloxyethyl phosphorylcholine (MPC) was spin-coated onto the array  
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13 1014 before drying in a convection oven. WCA proved the superhydrophilicity of the modified CA  
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17 1015 surface, with angles decreasing from 70° to 9°. Antibiofouling properties were evaluated against *E.*  
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20 1016 *coli* and *B. subtilis* suspensions in which they were incubated for 3 to 30 hours before live/dead™  
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23 1017 staining for fluorescence microscopy observations. Quantitative assays were also performed to  
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27 1018 confirm the antibacterial effect of the optically transparent substrates. The decrease of the density  
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30 1019 of detectable bacteria in fluorescence microscopy was mainly attributed to the chemical  
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33 1020 modification with MPC, while the live/dead™ staining assay confirmed that the nanoneedles were  
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37 1021 responsible for the bactericidal effect, by penetrating or stretching the bacterial membrane.<sup>92</sup> The  
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40 1022 same team also modified poly(ethylene glycol) dimethacrylate (PEGDMA) nanoneedles which  
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43 1023 swell in wet conditions. Interestingly, they maintained their shape upon swelling, and similarly to  
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47 1024 the CA nanoneedles, the best antibiofouling effect was obtained for the sample that combined the  
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50 1025 chemical surface modification and the presence of nanoneedle topography. With the intrinsic  
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53 1026 antibiofouling properties of PEGMA, MPC-PEGMA nanoneedle hybrids proved to be tough  
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4 1027 antibiofouling surfaces as a local destruction of the topography or zwitterionic MPC coating was  
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7 1028 not sufficient to totally impede the antiadhesive properties of the substrates.<sup>93</sup>  
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11 1029 Intraocular lenses have also been modified to avoid bacterial infection and minimize corneal cell  
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14 1030 attachment after cataract treatment. The lenses were altered by depositing a polymeric nanopillar  
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18 1031 array covered with ionic antibacterial polymer. The nanopillar array was produced by stamping a  
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21 1032 mix of polyurethane (PU) and Norland Optical Adhesive 63 polymer (PU/NOA63), onto a mold  
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24 1033 designed by photolithography. Then, iCVD was used to deposit a 50 nm thick layer of a copolymer  
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28 1034 of 4-vinylbenzyl chloride and 2-(dimethylamino)ethyl methacrylate. Thus, quaternary ammonium  
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31 1035 compounds (QACs) were introduced onto the surface of nanopillars. The antibacterial efficiency  
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34 1036 was measured against *S. aureus*. The nanopillar array alone demonstrated a 50% efficiency  
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38 1037 compared to flat PU/NOA63 polymer film, but it is only with the copolymer deposited on top that  
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41 1038 the antibacterial efficiency risen to almost 100%, confirming a profitable synergy between surface  
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45 1039 topography and chemistry. Upon adhesion, bacterial cells were captured in between the nanopillars,  
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48 1040 causing the latter to bend. The QACs available at the surface of the nanopillars are known to  
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51 1041 destabilize the bacterial membrane. When the nanopillars gradually restore their upright  
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55 1042 orientation, the bacteria slide down, and their membrane suffers deformation and then rupture.  
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3 1043 However, the engineered substrate showed biocompatibility for up to 7 days towards human  
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7 1044 corneal endothelial cells.<sup>94</sup>  
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#### 10 1045 **4. Conclusion & perspectives**

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15 1046 As we have seen throughout this study, biofilm is a problem encountered in many different  
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18 1047 applications, ranging from medical devices to the marine industry. With antibioresistance and  
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21 1048 biocide resistance on the rise, and World Health Organization urging to take action, new  
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25 1049 antibacterial and antibiofouling strategies need to be developed. Concern is also arising over the  
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28 1050 toxicity of bactericidal nanoparticles or metallic compounds, making the use of such substances  
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31 1051 questionable. Thus, combining other solutions such as organic polymers and topography can be an  
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35 1052 efficient mode of action.  
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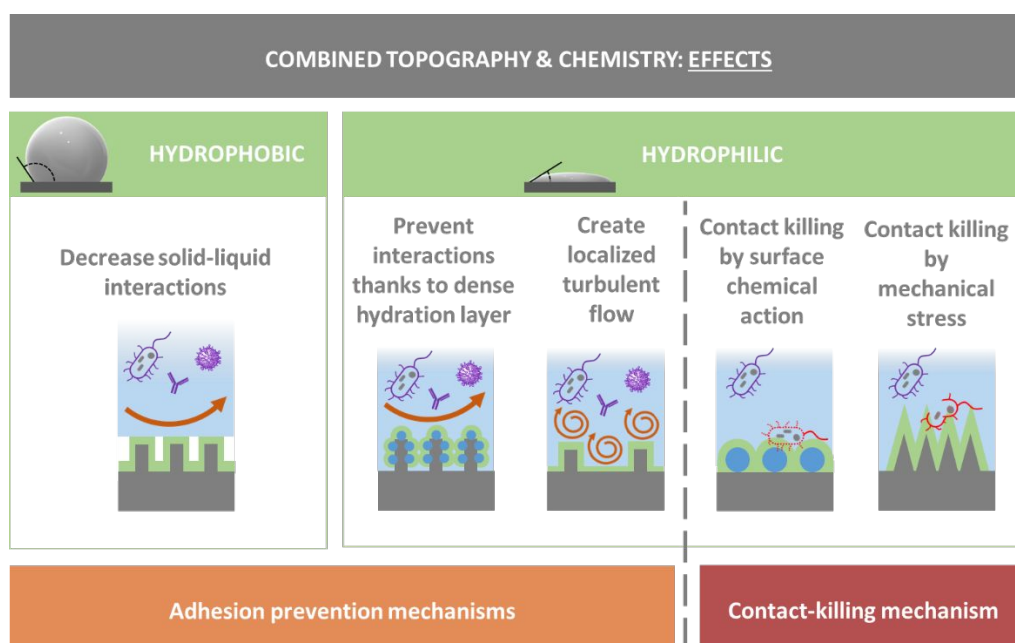
39 1053 More precisely, macromolecules with hydrophobic or hydrophilic properties show great interest  
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42 1054 for their ability to stop bacterial adhesion, and their activity can be enhanced by coating them on  
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46 1055 micro or nanostructured surfaces. In addition to increasing the wettability effect of certain  
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49 1056 substances, some structured surfaces can cause bacterial membranes to rupture through mechanical  
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53 1057 deformation. Others can lead to hydrodynamic fluxes which inhibit bacterial sedimentation and  
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4 1058 thus, biofouling. Precise control over the size and shape of the used structures could enable better  
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7 1059 understanding of their effect on bacterial adhesion and could also facilitate the adaptation of the  
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10 1060 surfaces to different strains of bacteria. Some structures could have opposite and non-desired  
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13 1061 effects and serve as bacterial traps. Concerning hydrophilic substances, depending on their nature,  
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17 1062 bactericidal properties can also be observed. All of these mechanisms are represented in Figure 15  
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20 1063 which highlights the diversity of action of hydrophilicity-based approaches in comparison to  
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23 1064 hydrophobic strategies based on the Cassie-Baxter regime.

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28 1065 As emphasized by the organisation of this review, the initial material used for creating these  
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31 1066 antibiofouling surfaces with a combined approach can be metallic, glass or a variety of polymers.  
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34 1067 The adaptability to various substrates is interesting to address the wide range of applications where  
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38 1068 antibiofouling surfaces are needed.

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42 1069 However, despite all the different solutions discovered while writing this review and summarized  
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45 1070 in Table S2 and S3, there seems to be a lack of statistical experiments. Indeed, here, independent  
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49 1071 experiments have been carried out with one combination of polymer and topography and one or  
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52 1072 two species of bacteria. This lack of systematic studies has been noticed by other teams and projects  
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56 1073 are arising. Indeed, Linklater *et al* have published in February 2022 a first statistical study of the

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4 1074 effect of different nanopillar polymers on *P. aeruginosa* and *S. aureus*.<sup>95</sup> Furthermore, oppositely  
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7 1075 to *in vitro* experiments, in natural environments, one species of bacteria, or one marine species is  
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10 1076 rarely found alone, rather in a mixture with many other organisms. Only a few of the articles in this  
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13 1077 review have mentioned experiments carried out with natural samples. Therefore we can wonder  
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17 1078 whether transposing any of these modified surfaces to other applications would prove efficient or  
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20 1079 if the substrate would always have to be adapted to the field of interest and to the particular device.  
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1081 *Figure 15: Diverse effects of surface modification approaches for antibiofouling, and corresponding*  
1082 *mechanisms*

1083 To verify the biocompatibility of these surfaces created with the prospect of replacing possible  
1084 toxic solutions, cytotoxicity experiments need to be carried out in parallel. This aspect can be

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4 1085 critical in some domains such as medical implants, where a risk of damaging human cells is  
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7 1086 unconceivable. It is also important in the marine industry to protect the natural fauna and flora. In  
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10 1087 this review, most of the publications using hydrophobicity to inhibit biofilm formation use fluorine-  
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13 1088 based chemicals. However, concern over the negative impacts of some fluorine-containing  
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17 1089 compounds could lead to an increase in fluorine-free surface development in the near future.  
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21 1090 Finally, the question of the robustness and durability of these surfaces should also be studied to  
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24 1091 verify their applicability *in vivo*. Indeed, biofilm is created rapidly but becomes stronger overtime.  
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28 1092 For a device left in a liquid medium over several months, it is very important that its efficiency  
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31 1093 does not degrade in that time. These durability assays should also be adapted depending on the  
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34 1094 application as the stress applied to a device could be very different.  
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39 1095 Overall, although complimentary research still needs to be carried out to respond to the yet  
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42 1096 unanswered questions, combining chemistry and topography seems to be a promising strategy to  
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46 1097 reach environmentally friendly, biocompatible and antibiofouling surfaces.  
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50 1098 SUPPORTING INFORMATION:  
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3 1099 Table S1 showing recent review articles on antibiofouling surfaces and overview tables (S2 & S3)

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7 1100 summarizing the combined strategies described in this manuscript.

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13 1102 **AUTHOR INFORMATION**

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33 1107 **Author Contributions**

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35  
36 1108 The manuscript was written through contributions of all authors. Miss Whiteley and Mr. Durand

37  
38  
39 1109 were in charge of the gathering and analysis of the relevant articles, and of the writing of the

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43 1110 manuscript. Mr. Mailley participated in the reviewing process and brought insights for the

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46 1111 manuscript structure, in addition to corrections. Mr. Nonglaton participated to the development of

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49 1112 the manuscript structure and scope, in addition to corrections. All authors have given approval to

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53 1113 the final version of the manuscript.

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4 1114 ‡These authors contributed equally.  
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12 1116 **Notes**  
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24 1121 **ABBREVIATIONS**  
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28 1122 *Abbreviations are all explained in the text*  
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32 1123 **REFERENCES**  
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