

# 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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9 10 11 12 13	2	antibiofouling surfaces – a review
14 15 16 17 18	3	AUTHORS.
19 20 21 22 23	4	Hippolyte Durand‡*, Amelia Whiteley‡, Pascal Mailley, Guillaume Nonglaton
24 25 26 27	5	
28 29 30 31	6	ADRESS.
32 33 34 35	7	Univ. Grenoble Alpes, CEA, LETI, DTBS, F-38000 Grenoble
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12	ABSTRACT. Despite decades of research on the reduction of surface fouling from biomolecules
13	or micro-organisms, the ultimate antibiofouling surface remains undiscovered. The recent covid-
14	19 pandemic strengthened the crucial need for such treatments. Among the numerous approaches
15	that are able to provide surfaces with antibiofouling properties, chemical, biological and
16	topographical strategies have been implemented for instance in marine, medical or food industries.
17	However, many of these methods have a biocidal effect and, with antibioresistance and biocide
18	resistance a growing threat on humanity, strategies based on reducing adsorption of biomolecules
19	and micro-organism are necessary for long-term solutions. Bio-inspired strategies, combining both
20	surface chemistry and topography, are currently at the heart of the best innovative and sustainable
21	solutions. The synergistic effect of micro/nano-structuration, together with engineered chemical or
22	biological functionalization is believed to contribute to the development of antibiofouling surfaces.
23	This review aims to present approaches combining hydrophobic or hydrophilic chemistries with a
24	specific topography to avoid biofouling in various industrial environments and healthcare facilities.
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## 1. Introduction

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

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



*Figure 1: Three antibiofouling mechanisms linked to corresponding types of surface modification. The* 

83	thickness of the links gives an estimation of the amount of research articles on the topics.
84	(i) In order to fight surface fouling with a limited quantity of antibiotics or biocides, a first
85	mechanism is active molecule releasing-surfaces. Antibiotic and biocide release will kill the micro-
86	organisms before they reach the surface and form biofilms. The release can be spontaneous in
87	active molecule surface loading approaches, or triggered by a specific physico-chemical stimuli
88	(pH, temperature, UV irradiation, enzymatic activity) in responsive surface approaches.
89	However, these approaches are limited in time, only affect micro-organisms and do not prevent
90	biomolecular fouling, and still face the issue of antibioresistance, biocide resistance and damage to
91	the environment. Only short term specific applications will benefit from this mechanism. <sup>3,13,14</sup>
92	(ii). A second mechanism relies on contact-killing. Surface chemistry approaches allow
93	immobilization of active molecules onto the surface, leading to micro-organisms being killed upon
94	contact or adhesion. In <i>responsive surface</i> approaches, the immobilized active molecule action can
95	be triggered upon a specific physico-chemical stimuli. Some responsive surfaces are also able to
96	eliminate the accumulation of dead cells that would progressively impede their contact-killing
97	effect. But this contact-killing effect can also be obtained without the use of active molecules.
98	Inspired by numerous natural surfaces in plants and the animal kingdom, engineered surface

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99	topography (nanopillars, microblades, nanospikes) is able to, in some cases, cause mechanical
100	stress on adhered micro-organisms, leading to membrane failure and eventually cell death. <sup>15–17</sup>
101	Hence, combined surface topography and chemistry approaches are also able to achieve contact-
102	killing mechanism, with potential synergistic effects that are reviewed in this manuscript.
103	(iii). At last, only the adhesion prevention mechanism prevents both biomolecules and micro-
104	organism fouling since they are engineered to prevent the interaction between the foulants and the
105	surface. For instance, superhydrophobic surfaces obtained by surface chemistry or combined
106	topography and chemistry approaches will avoid surface fouling since the foulants are confined to
107	the liquid phase which has a limited contact area with the surface. Similarly, zwitterion molecules
108	or polymers can provide surfaces with superhydrophilic properties, forming a dense hydration layer
109	that can also prevent fouling. Plus, depending on physico-chemical stimuli, responsive surface
110	approaches offer similar adhesion prevention mechanisms. <sup>18–20</sup>
111	
112	All these surface modifications tune the surface properties in terms of topography and/or chemical
113	composition. Moreover, the still on-going study of natural surfaces in plants, insects and the animal

3 4 5	114	kingdom have revealed numerous natural antibiofouling strategies that rely on the combination of
6 7 8	115	a specific surface topography with a particular surface chemistry. The published literature over the
9 10 11 12	116	past 5 years offers approximately five hundred reviews on the antifouling topic. Within this
13 14 15	117	overwhelming amount of review articles that cover the afore-mentioned antibiofouling
16 17 18	118	mechanisms, approximately 60 of them were selected based on their title and abstracts. They were
19 20 21	119	classified in table S1 of the Supporting information, according to the type of surface modification
22 23 24 25	120	approach detailed in Figure 1 (active molecule surface loading, surface chemistry, surface
26 27 28	121	topography, responsive surface and combined topography and chemistry). Less than ten mention
29 30 31	122	combined topography and chemistry approaches, and never as the core topic of the review. <sup>4,21–27</sup>
32 33 34 35	123	Up to our knowledge, none of them specifically focused only on this approach. This manuscript
36 37 38	124	aims to fill this gap and provide these works with their own specific review. However, these
39 40 41	125	research articles are not easily identified since authors do not always indicate the combined aspect
42 43 44 45	126	of their surface modifications. The research projects described in this review were then selected by
46 47 48	127	using three successive filters: firstly, surface topography approaches over the last 5 years were
49 50 51	128	explored. Secondly, the articles in which surface chemistry was used to complement the surface
52 53 54 55	129	topography were isolated. And thirdly, only the works that exposed the engineered surfaces to
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30 biomolecular and/or micro-organisms fouling were selected. Even if they can be sometimes a 31 source of inspiration for developing antibiofouling surfaces, research topics such as anti-corrosion 32 or self-cleaning surfaces, were mainly left aside. The in-depth analysis of the selected works led to several levels of classification following a 33 34 bottom-up process, as detailed in Figure 2. The first one is the nature of the substrate that is to be provided with antibiofouling property: metals and their oxides and hydroxides, glass and silicon-35 36 based materials, and polymers. Secondly, the articles are classified depending on the method used 37 to tune the substrate topography (step 1), either by modifying the substrate itself (endogenous 38 topography), or by using an additive strategy and adding another material (exogenous topography). 39 The third level relates to the surface chemistry modification: a vast majority of approaches 40 complement the topography with a chemical layer (step 2), but some approaches simultaneously 41 tune the substrate topography while producing the chemical layer (step 1&2).



	150	very limited amount of chemical entities are used: fluorine-based moieties and alkyl chains have
	151	been used for a long time in order to produce hydrophobic and superhydrophobic surfaces. More
0 1	152	recently, surfaces infused with silicon oils have been developed and used as self-cleaning surfaces
2 3 4 5	153	(often referred as slippery liquid infused surfaces, SLIS). Some research teams also used them in
6 7 8	154	antibiofouling applications. Conversely, for hydrophilic approaches, chemical entities are
9 0 1	155	numerous as exposed on Figure 2. Ranging from simple functional groups such as amine or
2 3 4 5	156	carboxylic acids to polymers and ionic compounds, hydrophilic approaches are at the heart of
6 7 8	157	today's most innovative antibiofouling research works. This manuscript is thus separated into two
9 0 1	158	chapters, the first one detailing the hydrophobic approaches, and the second one focusing on the
2 3 4	159	hydrophilic ones. This review is written from an applicative engineer perspective, the sub-chapters
6 7 8	160	are thus organized according to the nature of the surface to be treated: metals, glass and silicon-
9 0 1	161	based or polymers. The conclusion and outlook will provide the reader with recommendations
2 3 4	162	regarding further development of antibiofouling surfaces.
5 6 7 8 9	163	2. Combined topography and hydrophobicity for adhesion prevention
0 1 2	164	A majority of topographical hydrophobic approaches use fluorine-based compounds as a chemical
5 4 5 6 7	165	layer to increase the hydrophobicity. This is why the subchapter will not be organized regarding
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3 4 5	180	based samples and polymers. In addition, a few studies introduce approaches that are compatible
6 7 8	181	with various substrate types. A specific subchapter is dedicated to them. All the approaches are
9 10 11 12	182	detailed in Table S2 of the Supplementary information.
13 14 15	183	2.1. Metallic substrates
10 17 18 10	184	Metallic surfaces that are potentially exposed to biofouling are encountered in various fields of
20 21 22 23	185	activity, such as marine industry, food preparation facilities and healthcare.
23 24 25	186	2.1.1. Endogenous topography: micro/nanostructure designed from the
26 27 28	187	metallic substrate
29 30 31	188	In order to tune the topography, the most straightforward methods rely on the direct modification
32 33 34	189	of the metals surface itself. Micro/nanostructure can be produced through different approaches of
35 36 37 38	190	aqueous phase treatments and etching techniques which provide the surface with engineered
39 40 41	191	topography. These micro/nanostructures are referred as endogenous topographies.
42 43	192	2.1.1.1. Aqueous phase treatment
44 45	172	
46 47 48	193	A simple way to modify the topography of metallic substrates is the formation of oxide and
49 50 51	194	hydroxide layers at their surface. Upon immersion in boiling water, acidic or alkaline solutions or
52 53 54 55	195	a combination of these, metallic oxides, that are produced at the surface of the substrates, form
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3 4 5	196	hierarchical structures. Aluminium, magnesium or copper substrates are predominantly represented
6 7 8	197	in the following reviewed articles. Using a subsequent step of chemical surface modification with
9 10 11 12	198	hydrophobic compounds, some research teams managed to use combined topographical and
12 13 14 15	199	chemical approaches to obtain superhydrophobic substrates. For instance, commercial aluminium
16 17 18	200	sheets were enhanced with hierarchical micro/nano topographies produced by strong acid etching
19 20 21	201	followed by immersion in boiling water. Subsequently, 1H,1H,2H,2H-
22 23 24 25	202	perfluorodecyltrichlorosilane also known as FDTS was used to chemically functionalize the
26 27 28	203	structured Al surfaces, as depicted on Figure 4A. <sup>30</sup> During boiling water treatment, the average
29 30 31	204	roughness increased from 5 to 65 nm with the formation of Bohemite under the form of
32 33 34 35	205	nanoplatelets on top of the existing microprotusions. Only the combination of micro and nanoscale
36 37 38	206	roughness with hydrophobic silane grafting provided the surface with superhydrophobic properties
39 40 41	207	which resulted in a drastic decrease of bovine serum albumin (BSA) adsorption. An 80% relative
42 43 44 45	208	reduction in adhered bacteria was measured, regardless of the bacterial strain and their outer layer
46 47 48	209	properties (Pseudomonas aeruginosa, Staphylococcus epidermidis, and Staphylococcus aureus).
49 50 51	210	Finally, cytotoxicity of the samples was assessed through MTT assay and relative complete cell
52 53 54 55	211	compatibility (HeLa cells) was validated, confirming the benefits of such a treatment for <i>in vivo</i>
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	212	applications. More recently, Mandal and co-workers studied the modification of an aluminium
	213	alloy through micro-imprinting to obtain square micropillars, followed by hot water treatment
D 1	214	which covered the pillars with flake-like AlO(OH) bohemite nanostructures. Finally, a perfluoro-
2 3 4 5	215	silane layer was deposited by chemical vapor deposition (CVD) on top on the nanostructure. The
5 7 8	216	superhydrophobic Cassie-Baxter regime was achieved and allowed for a drastic decrease of
9 0 1	217	<i>Escherichia coli</i> growth. <sup>31,32</sup>
2 3		
4 5 5	218	Copper hydroxide can also be produced to tune the surface topography. A copper mesh was
7 8 9	219	modified through the formation of $Cu(OH)_2$ nanowires at its surface, followed by Cu based metallic
) 1 2	220	organic framework (MOF) production and finally polydimethylsiloxane (PDMS) deposition on the
3 4 5	221	micro/nano structure as depicted in Figure 4B. Hierarchical mushroom-like structures were
5 7 8 9	222	obtained as confirmed by scanning electronic microscopy (SEM) images. Water contact angles
2 1 2	223	above 150° and sliding angles below 4° were measured. Antifouling and self-cleaning properties
3 4 5	224	were validated against products such as, milk, coffee, tea, cola and juice. In addition, dirt and salts
5 7 8 9	225	were easily removed from the substrate leaving no trace. But more importantly, drag reduction also
) 1 2	226	benefited from the treatments applied to the Cu mesh, making it a promising material for innovative
3 4 5	227	marine vehicle development. <sup>33</sup>



#### **ACS Applied Bio Materials**

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243 formation of small flocules and a WCA of 157.3°, confirming superhydrophobicity (see Figure 5A). A 1-log reduction of bacterial growth was observed for *E. coli* (about 90% inhibition), a 2-244 245 log reduction was obtained against S. aureus, for which an inhibition efficacy of over 99% could 246 be observed. The difference in bacterial membrane structure between Gram positive and Gram 247 negative is used to explain this result. To assess the long-term use of theses substrates, abrasion tests were carried out with sandpaper, and 6-month storage in air also took place. Neither of these 248 249 experiments considerably affected the properties of the surfaces. 250 Taking inspiration from lotus leaves, Zouaghi and co-workers used femtosecond laser ablation onto 251 stainless steel surface to produce micro and nano topography. Here, the surface was coated with a 252 perfluorosilane in an organic solvent, resulting in a first combined approach called LL (lotus-253 like).<sup>37</sup> A second approach consisted in impregnating this LL substrate with an perfluorinated oil 254 in order to obtain a slippery liquid infused surface (SLIS) also known as SLIPS (for slippery liquid 255 infused porous surface), as depicted in 256 Figure 5B. Antibiofouling tests were performed in a pilot pasteurizer with a model fluid composed 257 of 1 wt% of whey protein, in a temperature range representing dairy industry conditions (65-85 $^{\circ}$ C). 258 Although a complete suppression of fouling was observed for SLIPS, an increase in fouling was

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



3 4 5	279	imaging revealed the micro and nano-sized topographical features. Chemical characterization with
6 7 8	280	energy dispersive spectroscopy confirmed the homogeneous covering with the spraying technique.
9 10 11 12	281	The wettability was evaluated against several different liquids (water (pH 0 and 14), ethanol
13 14 15	282	solutions, rapeseed oil, ethylene glycol, propylene glycol and cyclohexane) that all reached contact
16 17 18	283	angles above 150°, confirming superamphiphobic properties. The combination of surface
20 21 22	284	topography and hydrophobic chemistry leads to antifouling properties and has potential drag-
23 24 25	285	reduction properties. Moreover, the mechanical robustness of the coating was confirmed after
26 27 28 29	286	abrasion tests which led to a very small loss of super-amphiphobic properties. The micro
30 31 32	287	topography withstood the abrasion and both nano topography and chemical functions were
33 34 35	288	preserved. <sup>39</sup>
36 37 38 39	289	2.1.1.3. Reactive ion etching
40 41 42	290	Reactive ion etching (RIE) was implemented on stainless steel by Cao and co-workers to produce
43 44 45	291	rectangular micropillars with different arrangements and spacing. A peptide coating was applied
46 47 48 49	292	through immersion, and resulted in a hydrophobic surface that decreased the adhesion of marine
50 51 52	293	algae Chlorella pyrenoidosa and Phaeodactylum tricornutum. The synergy between topography
53 54 55 56	294	and chemical peptide layer was confirmed. <sup>40</sup> High power electro-etching in sodium chloride
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295 solution has also been used to produce micropillars on stainless steel surface, followed by vapor 296 deposition of various FDA-approved food-contact coatings: Ni-P-PTFE, Lectrofluor® 641, CrN, 297 TiN, and Dursan®. Among them, the patented Dursan® coating process offered the most 298 promising fouling resistance against L. monocytogenes, but the combination with micropillars gave 299 roughly the same results as on flat samples.<sup>41</sup> 300 2.1.2. Exogenous topography: micro/nanostructure through additive 301 strategies on metals 302 Additive strategies give access to more diverse topography geometries. By incorporating various 303 micro or nano objects to the metallic surface, some research teams developed antibiofouling 304 surfaces with more complex topographies. These are referred to as exogenous topographies. 305 Electro-deposition. 2.1.2.1. 306 By using a metallic substrate as an electrode, electro-deposition of diverse conducting substances 307 can be achieved. For instance, using copper foil as an electrode exposed to a phosphate containing 308 electrolyte, Bao et al produced microflower-like structures composed of copper and phosphate ions 309 complexes. Although no biological anti-fouling experiments were conducted, a superhydrophobic 310 self-cleaning and anti-corrosion surface was obtained after dodecylamine coating.<sup>42</sup> Inspired by

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3 4 5	311	similar research,, <sup>43,44</sup> the team of Chang-Hwan Choi chose aluminium foil to be anodized in an
6 7 8	312	oxalic acid solution to obtain a nanoporous structure that was thinned down with phosphoric acid
9 10 11	313	treatment, resulting in disconnected nanopillars. After evaporation under controlled conditions,
12 13 14 15	314	clusters of nanopillars assembled into conical nanostructures. A Teflon <sup>TM</sup> coating was finally
16 17 18	315	applied to obtain a superhydrophobic surface (Figure 6A) which was submitted to biofouling tests
19 20 21	316	against <i>E. coli</i> and <i>S. aureus</i> in static and dynamic conditions. <sup>45</sup> Up to 4-log reductions were
22 23 24 25	317	obtained upon bacterial adhesion testing for conical pillars covered with Teflon <sup>TM</sup> only, confirming
26 27 28	318	the synergy between the nanotopography and surface chemistry. A more recent study used
29 30 31	319	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O electrolyte to create flower-like nanosheets through electro deposition onto
32 33 34 25	320	polished E40 steel. The treatment was followed by high vacuum sputtering of PTFE and resulted
36 37 38	321	in a superhydrophobic micro/nano structured PTFE/WO <sub>3</sub> coated E40 steel substrate (Figure 6B)
39 40 41	322	with anti-pollution, anti-icing and antibiofouling properties (also obtained on Cu, Mg and Ti
42 43 44	323	alloys). She wanella algae adhesion was completely avoided over 14 days immersion in the bacterial
45 46 47 48	324	suspension, while raw E40 steel and PTFE coated steel were covered with bacteria. The
49 50 51	325	superhydrophobicity and electrostatic repulsion arising from the synergistic combination of
52 53 54	326	micro/nano-structure and PTFE coating are believed to explain such results. <sup>46</sup> However, the $WO_3$
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coated-only steel was not part of the antifouling characterized samples. It could have helped to

better distinguishing contributions of micro/nano-structure vs chemical surface composition for

explaining antibiofouling results. Ouyang and co-workers grew dendritic Ag micro/nanostructures

through Ag electro-deposition onto Titanium substrates, followed by dodecanethiol vapor

deposition and dimethyl silicone oil infusion to produce a Slippery Liquid-Infused Porous Surface

(SLIPS) (Figure 6C). A reduction by 4 orders of magnitude of diatom Navicula minima and green

algae *Chlorella vulgaris* was achieved upon 14 days of incubation.<sup>47</sup>

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347	growth were investigated against <i>Pseudomonas aeruginosa</i> PAO1 and <i>Listeria monocytogenes</i> CIP
348	103574 (commonly found in medical facilities and food industry environments). The smallest value
349	of deposition charge (1 mC.cm-2, without nanofibers), did not reduce the bioadhesion. On the
350	contrary, higher deposition charge (35 mC.cm <sup>-2</sup> ), producing expanding vertical nanofibers, reduced
351	the bioadhesion by 3-4 log. This result confirmed that the superhydrophobic chemistry alone was
352	not enough to reduce the bacterial bioadhesion. A proiminent surface topography was necessary to
353	achieve bacterial adhesion reduction. Biofilm growth was also performed and biofilm biovolume
354	were measured. The same conclusions arised on the importance of surface topography to limit
355	biofilm development.
355 356	biofilm development. 2.1.2.2. Other methods
355 356 357	biofilm development. 2.1.2.2. Other methods Leaving aside electro-deposition, the next three articles use different exogenous methods to create
355 356 357 358	biofilm development. <b>2.1.2.2.</b> Other methods Leaving aside electro-deposition, the next three articles use different exogenous methods to create topography. The first approach relies on the production of layered double hydroxide (LDH) films.
<ul> <li>355</li> <li>356</li> <li>357</li> <li>358</li> <li>359</li> </ul>	biofilm development. <b>2.1.2.2.</b> Other methods         Leaving aside electro-deposition, the next three articles use different exogenous methods to create         topography. The first approach relies on the production of layered double hydroxide (LDH) films.         Aluminium alloys were coated with lithium-aluminium (Li-Al) LDH films. This is known as
<ul> <li>355</li> <li>356</li> <li>357</li> <li>358</li> <li>359</li> <li>360</li> </ul>	biofilm development. <b>2.1.2.2.</b> Other methods         Leaving aside electro-deposition, the next three articles use different exogenous methods to create         topography. The first approach relies on the production of layered double hydroxide (LDH) films.         Aluminium alloys were coated with lithium-aluminium (Li-Al) LDH films. This is known as         hydrotalcite preparation. The samples were functionalized with 4-amino-2-((hydrazine methylene))
<ul> <li>355</li> <li>356</li> <li>357</li> <li>358</li> <li>359</li> <li>360</li> <li>361</li> </ul>	biofilm development. <b>2.1.2.2.</b> Other methods Leaving aside electro-deposition, the next three articles use different exogenous methods to create topography. The first approach relies on the production of layered double hydroxide (LDH) films. Aluminium alloys were coated with lithium-aluminium (Li-Al) LDH films. This is known as hydrotalcite preparation. The samples were functionalized with 4-amino-2-((hydrazine methylene) amino)-4-oxobutanoic acid (AOA) and 1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -perfluorooctyltriethoxysilane (PFOTES).

3 4 5	363	SEM analysis showed a nest-like rough structure for these films with vertically-grown crosslinked
6 7 8	364	nanoplates. These films showed good anti-adhesive properties towards <i>E. coli</i> , <i>Bacillus subtilis</i> and
9 10 11	365	sulfate reducing bacteria, with repellency over 96% for each species. Antibacterial activity against
12 13 14 15	366	Gram-positive, Gram-negative and anaerobic bacteria is provided by the guanadino group of the
16 17 18	367	AOA. Combined with the surface roughness and hydrophobicity, this leads to surfaces with high
19 20 21 22	368	antibiofouling capacities. Using atmospheric pressure plasma spraying (APPS), the liquid
22 23 24 25	369	precursor hexamethydisiloxane was deposited onto foodgrade stainless steel. Process parameters
26 27 28	370	were studied in a first paper which revealed the influence of the precursor flow on the surface
29 30 31 32	371	roughness and morphology of the resulting coated surface (denoted as PL). <sup>37</sup> This refers to the <i>Step</i>
33 34 35	372	1&2 Simultaneous topography and chemistry approach described on Figure 2. The particular
36 37 38	373	chemical surface composition, combined with the random nanostructures revealed by atomic force
39 40 41	374	microscopy (AFM), led to a strong reduction of fouling upon two consecutive runs in a pilot
42 43 44 45	375	pasteurizer. A second study was conducted to compare this PL sample with lotus-like (LL) and
46 47 48	376	SLIPS samples that were described earlier in the previous <i>endogenous</i> section. Upon the fouling
49 50 51	377	test in the pasteurizer, LL and SLIPS surfaces failed to overcome the durability of PL surfaces over
52 53 54 55	378	the two consecutive runs. <sup>38</sup> Different bacterial strains were tested on PL samples only and
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compared to bare stainless steel surface: a very mild reduction of <i>S. aureus</i> adhesion was observed
but a strong reduction of bacterial adhesion for rod-shaped bacteria was obtained: 58% and 80%
for <i>L. monocytogenes</i> and <i>Salmonella enterica</i> respectively. The round-shaped bacteria are able to
penetrate into the microspaces of the grain structures of the PL surface, while rod-shaped bacteria
cannot, and thus have less anchoring spots, leading to reduced adhesion. However, authors did not
discuss the viable or dead state of the adhered bacteria that usually allow for further understanding
of the anti-adhesion and/or contact bactericidal effect.
Finally, Selim and co-workers used alumina or zinc nanorods associated with PDMS on steel in
order to fight against marine fouling. In a first study, graphene oxide-alumina nanorod hybrid
sheets were enhanced with exfoliated PDMS chains. The optimal amount of 1 wt% nanofiller
389 ensured the best dispersion of the nanoparticles. The resulting coating exhibited
superhydrophobicity and fouling resistance. After 28 days <i>in vitro</i> exposure to <i>Micrococcus sp</i>
(Gram-positive), <i>Pseudomonas putida</i> (Gram-negative) or <i>Aspergillus niger</i> (fungus), a sharp
reduction of cell viability was observed. Fouling resistance was also confirmed with a three-month
field assay in marine waters. <sup>50</sup> In another study, zinc oxide nanorods were embedded in a PDMS
matrix to produce a similar superhydrophobic coating on steel. The same bacteria and fungus were
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395 used for fouling resistance tests and, again, an optimized amount of nanofiller was detected at 0.5% 396 above and below which the properties were lost. A 6-month field trial assay in natural seawater 397 confirmed the *in vitro* tests. In both of these studies, the micro/nano-roughness combined to low 398 energy surface chemistry is called to explain the results.<sup>51</sup>

## 2.2. Glass and silicon substrates

400 Regarding glass and silicon substrates, fewer articles dealing with combined topography and 401 chemistry approaches were encountered. The first one uses endogenous topography, produced 402 through laser patterning, while the second one uses both endogenous (reactive ion etching) and 403 exogenous topography with addition of another material (crystal seading). All the others use 404 different exogenous topographies.

405 Lee *et al* addressed biofouling on endoscope lenses. In order to prevent bacterial infection and 406 fogging while achieving high mechanical durability, the lens was provided with a lubricant-infused 407 directly engraved nano/micro-structured surface (LIDENS).<sup>52</sup> Femtosecond laser patterning was 408 first applied to the devices to obtain nanostructured surfaces. A coating of fluorinated self-assembly 409 monolayer was then added before infusion of the perfluorocarbon-based lubricant whose affinity 410 with the surface is increased with the fluorocarbon chains (see Figure 7A). The LIDENS coating

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411 showed very good anti-adhesive effects towards blood which rolled off the surface without leaving 412 any trace. Fluorescent microscopy also demonstrated low adhesion towards albumin and 413 fibrinogen. In addition, tape-peeling and linear abrasion tests confirmed the robustness of the 414 LIDENS coating. 415 The next approach engraved the raw substrate to create micro-topography (endogenous), but also 416 used a new material to produce the nano-topography on top of it (exogenous). Inspired by the lotus-417 leaf effect, silicon wafers were subjected to RIE to produce micro-cylinders. Zinc oxide crystal 418 seads were then spincoated onto the microstructured surface allowing for the growth of Zinc salt 419 nanoneedles through low temperature hydrothermal reaction. Finally, a fluoroalkylsilane coating 420 was deposited by immersion in the silane solution, as depicted in Figure 7B. The resulting surface 421 exhibited superhydrophobicity with the Cassie-Baxter regime upon contact with liquid. A 99% 422 bacterial repellency was obtained even after 24h exposure to a bacterial suspension of *E. coli*, compared to the flat untreated silicon wafer.<sup>53</sup> Moreover, the few bacteria that eventually adhered 423 424 onto the substrates were easily killed by the nanoneedles, as confirmed by their shrunken 425 morphologies (obtained by SEM) and non-viable state (by live/dead<sup>TM</sup> staining). The combination

426 of a topographical approach and relevant chemical surface treatment produced a synergistic





437 chemistry.

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438	Silane chemistry is of primary interest when silicon-based substrates are to be chemically modified.
439	Privett et al used nanostructured fluorinated silica colloids, fluoroalkoxysilane (heptadecafluoro-
440	1,1,2,2-tetrahydrodecyl)-trimethoxysilane (17FTMS) and methyltrimethoxysilane (MTMOS) to
441	develop superhydrophobic xerogel coatings which showed anti-adhesive properties towards $S$ .
442	aureus and P. aeruginosa.55 The particles showed both micro and nanoscale size. Acid-catalysed
443	hydrolysis and condensation was then performed to obtain 17FTMS/MTMOS films with or without
444	particles. The synergic combination of colloids and the fluorinated xerogel resulted in a
445	superhydrophobic surface. Soaking in water over 15 days did not affect the WCA, suggesting the
446	coatings were stable. These surfaces reduced bacterial adhesion by 99% for S. aureus and $98.2\%$
447	for <i>P. aeruginosa</i> .
448	In addition to liquid phase chemistry, vapor phase approaches were also used to tune silicon-based
449	substrates. Hence chemical vapor deposition techniques are able to bring both the topography and
450	the chemistry. In the first example, glass slides were covered with a silicone elastomer film through
451	dip-coating and subsequent aerosol assisted chemical vapor deposition (AACVD) of Sylgard® 184
452	silicon elastomer. <sup>54</sup> This process allowed for the formation of micro-scale random topographic
453	features, as described in Figure 7C. The bacterial adhesion on modified glass slides was evaluated

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454	with <i>E. coli</i> and <i>S. aureus</i> through live/dead <sup>TM</sup> staining assay in 30 ml of $10^7$ colony forming unit
455	(CFU)/ml bacterial suspensions, maintained for 1 hour in static conditions. Non-adherent bacteria
456	were then removed and <i>BacLight</i> <sup>TM</sup> Bacterial Viability Staining kit was used to detect adhered
457	bacteria with fluorescence microscopy. The total amount of live and dead adhered bacteria was
458	drastically decreased on the modified glass slides, presumably because the aqueous bacterial
459	suspension is repelled by these surfaces.
460	An atmospheric plasma polymer coating was used to treat silicon wafers and produced a
461	microstructured topography while also imparting hydrophobic and superhydrophobic properties to
462	the surface, that prevent bacterial adhesion. <sup>56</sup> A mixture of docecyl acrylate and 1H,1H,2H,2H-
463	perfluorodecyl acrylate precursor was used. AFM imaging revealed a heterogeneous globular grain
464	structure. The wettability was studied with contact angle measurements to monitor the transition
465	from hydrophobic Wenzel regime to superhydrophobic Cassie-Baxter regime. The core of the
466	study lies in the fact that the authors performed statistical analysis to compare the influence of
467	different parameters on bacterial adhesion. These parameters were either related to the surface
468	(topography, chemistry, wettability) or to the bacterial medium in which the substrate was
469	incubated (bacteria species, culture, medium composition). The main result indicated that bacterial

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470 colonization is by far predominantly influenced by culture conditions rather than surface properties. 471 This input is precious for researchers that tackle antibiofouling surface development since it 472 encourages them to use various medium conditions to assess precisely the antibiofouling 473 properties. The second result indicates that the superhydrophobic substrates were the more 474 effective at preventing bacterial adhesion, even after static or hydrodynamic long term culture. This 475 type of statistical analysis of the influence of culture conditions could be done for every type of 476 surface treatment that is developed to fight bacterial fouling. **Polymer substrates** 2.3. 477 478 As for a few of the metallic substrates, the following approaches dealing with polymeric substrates 479 can be separated into endogenous and exogenous topography. Molding techniques and plasma 480 treatments are highly represented in the former category, while co-polymers and inorganic 481 structures are used in the latter to design the topography. 2.3.1. Endogenous topography: micro/nanostructure designed from 482 483 polymers 484 2.3.1.1. Molding 485 Polymers are soft matter compared to metal and silicon-derived materials. Topographical features 486 can thus be easily obtained with simple thermal treatment of molding/templating processes, as it is 33 59 ACS Paragon Plus Environment 60

described in the next studies. Inspired by the pitcher plant, Ware and co-workers tuned the

topography of Teflon<sup>TM</sup> coated on polyethylene substrates with a simple thermal treatment at 160°C

to produce micro-wrinkles in which a silicon oil was then infused. The resulting superhydrophobic

surface demonstrated a 99% adhesion inhibition against Pseudoalteromonas spp. bacteria. The

inhibition was still above 76% after 2 weeks exposure to seawater. A complementary field test was

performed for 7 weeks in the ocean and the surface was only covered at 23% when reference

samples were fully covered with marine fouling.<sup>57</sup> The article also contains a brief overview of a

dozen studies related to lubricant infused surfaces that were tested against biological foulants such

Dolid et al combined a shark-skin pattern on PDMS with a peptide-based coating to obtain

functional surfaces that repel bacteria.<sup>58</sup> A silicon wafer master produced by photolithography was

used to mold the structured shark-skin patterned surface, and a dopamine and peptide-based

mixture was then used to coat the PDMS substrates by a spraying technique, as depicted in Figure

8A. The water contact angle reached 119°. Upon testing against *E. coli* adhesion, it was shown that

the chemically and topographically modified surfaces reduced bacterial adhesion by 85% in

comparison to bare substrates. With S. epidermidis, adhesion reduction reached 72%. Dynamic

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2 3 4 5	503	assays were also carried out with <i>E. coli</i> and demonstrated that no adhesion occurred on the peptide-
6 7 8	504	coated and patterned substrates.
9 10 11	505	2.3.1.2. Plasma treatment
12 13 14 15	506	Plasma treatment can easily and rapidly modify the topography of polymers. In the next studies,
16 17 18	507	different plasma treatments are used to modify the topography of polymer substrates. Oxygen
19 20 21 22	508	plasma treatment is a very common process and can easily modify polymers' topography. But other
23 24 25	509	gases are able to form plasma, and their combination with fluorinated carbon compounds lead to
26 27 28	510	topography modification as well as hydrophobization.
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523 the prepared surfaces. The enhanced IOL was also as transparent and mechanically resistant as the 524 pristine IOL. Anti-bioadhesion and cell viability experiments as well as animal testing 525 complemented with statistical analysis were performed. Bioadhesion is reduced the most when 526 topography and the chemical liquid-like layer are used simultaneously. The same outcome was 527 confirmed for cell viability. After 60 days of *in vivo* experiments, the enhanced IOL demonstrated 528 excellent biocompatibility and anti-PCO effect. 529 Oxygen plasma micro/nano-texturation was also performed on poly(methyl-methacrylate) 530 (PMMA) transparent sheets. Combined with metal-sputtering and/or hydrophobic film deposition, antibiofouling and antimicrobial properties were obtained.<sup>60</sup> Two different hydrophobic coatings 531 532 were finally used: octafluorocyclobutane (C4F8) that was deposited through plasma again, and 533 perfluorooctyltrichlorosilane (pFOTS) through vapor deposition after oxygen plasma activation. 534 For this review, the focus here covers only the textured PMMA sheets modified with hydrophobic 535 coatings only (no metals). These samples were immersed in a bacterial suspension of unicellular 536 Gram-negative cyanobacteria Synechococcus sp. for 72 hours in order to study bacterial adhesion. 537 A resulting coverage of less than 1.5% was detected, suggesting efficient anti-adhesive properties. 538 However, the author did not discuss the potential synergistic effect of the micro/nano-texture and

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539 hydrophobic coatings. Experiments with hydrophobic coatings on PMMA without the micro/nano 540 texture would have helped on this matter.

541 Argon and Argon/CF<sub>4</sub> plasmas were used to modify polycarbonate substrates. The Argon/CF<sub>4</sub> 542 treatment imparted both topography and specific surface chemistry that reduced bacterial and 543 microalgae adhesion.<sup>61</sup> AFM measurements revealed that Ar plasma alone was not able to modify 544 the polycarbonate substrates topography. Only Ar/CF<sub>4</sub> plasmas increased the roughness 545 significantly. Bioadhesion tests were performed in flow-cells with bacterial (two Gram negative 546 marine bacteria, Paracoccus sp. 4M6 and Pseudoalteromonas sp. 5M6) and diatom (two axenic 547 microalgae strains, Cylindrotheca closterium AC-170 and Porphyridium purpureum AC-122) 548 cultures. Bacteria were exposed 2 h to the surface while 24 h exposure with 12 h-12 h light-dark 549 cycle was carried out with microalgae. The main outcome is that only the Ar/CF<sub>4</sub> treated 550 polycarbonate with higher content of  $CF_4$  managed to reduce the adhesion of the tested micro-551 organisms (65% to 90% reductions). The authors claim the combination of surface chemistry and 552 nano-topography explains such a result. The stability of the modified substrates was also evaluated 553 with contact angle measurements after 1 hour-treatment with 2.6% bleach, and no effect was 554 detected. 38 60

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# 2.3.2. Exogenous topography: micro/nanostructure through additive strategies on polymers

57 Polymer surface topography can also be modified by the deposition of a polymer of different

58 nature, but inorganic structures are also used as exogenous material to tune the topography.

59 Inspired by frog skin, this approach consisted in coating a PDMS layer with a block copolymer of 60 polystyrene (PS) and polylactic acid (PLA). Upon an hydrolytic treatment, the PLA blocks were 61 degraded generating microwrinkled surfaces due to the kinetic release of local strains along the 62 multilayer composite. In addition, the volumes freed from PLA blocks formed a nanoporous 63 structure with co-continuous nanochannels. Finally, a silicon oil was infused into the porous structure thanks to capillary forces in order to produce a wrinkled SLIPS.<sup>62</sup> Antibiofouling 64 65 properties were assessed against the green algae species *Chlorella* sp. DT through cell coverage 66 analysis after immersion in a suspension in static conditions for 7 days. Further evaluation was 67 performed in fresh seawater for 7 days with blue-green algae species (Arthrospira platensis and 68 Synechococcus lividus), seawater algae species (Isochrysis galbana, Tetraselmis ehui) and 69 filamental cyanobacteria under different culture conditions that mimick the natural environments 70 of these microorganisms. Without the silicon oil (topographical approach only), in static condition

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3 4 5	571	assays, antibiofouling performance was slightly improved when increasing wrinkle interspaces.
6 7 8	572	The author explains this tendency by indicating that the 15 $\mu$ m green algae has less attachment
9 10 11 12	573	points with increasing the wrinkle wavelength. However, performance dramatically improved after
13 14 15	574	silicon oil infusion, especially for the largest (75 $\mu$ m) wrinkle wavelength. This illustrates the
16 17 18	575	beneficial effects of the combination of both topography and chemistry for antibiofouling
19 20 21	576	performance. Testing in dynamic conditions lead to similar results. The authors also tested an oil-
22 23 24 25	577	infused substrate without the wrinkling structure (chemical approach only). Its performance was
26 27 28	578	lower than substrates with combined approaches. However, it appeared that the lubricant is hard to
29 30 31	579	retain in dynamic conditions. Finally, optical transparency, anti-icing and self-cleaning properties
32 33 34 35	580	were demonstrated for the wrinkled oil infused substrates, confirming their high potential for
36 37 38	581	sensors or optical devices in marine industry.
39 40 41 42	582	Another example of topography modification with added material relied on the growth of Nickel
43 44 45	583	hydroxide $Ni(OH)_2$ onto a cotton fabric, followed by immersion in stearic acid solution and thermal
46 47 48	584	treatment to produce nickel stearate broccoli-like micro-structures. The modified cotton fabric was
50 51 52	585	turned superhydrophobic (160°), and suppressed bacterial growth of Gram-positive <i>S. aureus</i> and
53 54 55	586	Gram-negative E. coli, as well as fungal growth of Candida albicans even if the antibacterial
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587	mechanism remains unclear (Ni <sup>2+</sup> release is suggested to play a role). <sup>63</sup> Cotton fabric was also
588	modified with $SiO_2$ nanoparticles enhanced with photodynamic activity of chlorin e6 (Ce6) and
589	functionalized with perfluoroalkyl-silane as described in Figure 9A. The textile's antibiofouling
590	property was evaluated against suspensions of Gram-positive S. aureus and Gram-negative E. coli.
591	Immersion and spraying in the dark were the two methods of exposure to the microorganisms,
592	modelling waterborne and airborne bacterial contamination, respectively. The synergistic effect of
593	superhydrophobic coating with perfluoroalkyl-silane and air trapping by hierarchical
594	nanostructures was proposed as an explanation for the significant reduction of bacterial adhesion
595	(ca. 90%) for both strains in the immersion approach. Similar results were obtained for the spraying
596	approach. Remaining bacteria elimination was expected to be eradicated by the photodynamic
597	activity of Ce6 that generates reactive oxygen species (ROS) upon visible light illumination. The
598	modified cotton textiles demonstrated a clear 100% killing rate against both S. aureus and E. coli
599	after 45 min of light illumination. Finally, modified textile fibers were exposed to whole blood and
600	managed to entirely repel the complex medium upon roll-off experiments. <sup>64</sup>



	613	9B). <sup>65</sup> Roll off angles below 6° were measured. Moreover, thermal and mechanical resistance were
	614	evaluated for an hour against ultrasonic treatment, or 85°C aqueous medium. Contact angles were
0 1	615	not affected at all. The performance of direct contact membrane distillation (DCMD) was
2 3 4 5	616	performed with the pristine and enhanced membranes. Model wastewaters were used: a mixture of
5 6 7 8	617	NaCl, CaCl <sub>2</sub> and NaHCO <sub>3</sub> or NaCl and sodium dodecyl sulfate. The superhydrophobic membrane
9 0 1	618	outperformed the pristine membrane in every case with delayed compromised flux and no salt
2 3 4	619	crystallization. Even after 60h long DCMD testing, the nanorods were still present and the
5 6 7 8	620	membrane still functional. According to the author, the clear contribution of both the structured
9 0 1	621	nanorods and the chemical fluor layer contributed to reach the Cassie-Baxter regime that prevents
2 3 4	622	membrane wetting and explains such results.
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8 9	623	2.4. Multi-substrate approaches
0 1 2	624	In this last subchapter the focus is given to the research articles that offer a combined topography
- 3 4 5	625	and chemistry approach for antibiofouling surface modification that have been successfully applied
6 7 8	626	to substrates of different nature. Indeed, from an applicative engineer perspective, such approaches
9 0 1 2 3	627	are of great interest since they might be used in various industrial fields, regardless of the nature of

the materials to be protected. These approaches inherently fall into the exogenous topography

category. A robust superhydrophobic coating was developed through the use of wrinkled fibrous nano silica functionnalized with octyltriethoxysilane (OTES), as depicted in Figure 10A. Various substrates (PVDF, glass, aluminium foil, fabric and paper) were treated with the wrinkled fibrous nano silica dispersions by spray (hard substrates) or dip coating (soft substrates). The superhydrophobicity was confirmed by contact angle measurements with daily liquid products such as honey, milk, coffee, yogurt and juice. The robustness of the coating was demonstrated through abrasion testing, finger wiping, tape adhesion and bending as well as before and after exposition to harsh environmental conditions (UV light, organic solvents and salts, high temperatures). Also, preliminary antifungal properties were revealed after exposition of a modified fabric to fungal species under favorable conditions. The combination of the hydrophobic properties with the surface roughness of the coral-reef like structure (and inherent air gaps) prevented the adhesion of micro-organisms and drastically reduced the availability of nutrient in the liquid phase close to the surface.66



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<ol> <li>26</li> <li>27</li> <li>28</li> <li>29</li> <li>30</li> <li>31</li> <li>32</li> <li>33</li> <li>34</li> <li>25</li> </ol>	644 645 646 647 648 649	Figure 10: Multisubstrates combined chemical and topographical approaches. A: wrinkled nano silica functionnalized with octyltriethoxysilane deposited on textile, aluminium foil, glass, PVDF, fabric and paper (adapted with permission from reference <sup>66</sup> , Copyright 2020 Elsevier). B: hot filament chemical vapor deposition for micro and nano sized diamond hemispheres, covered with perfluorosilane (adapted with permission from reference <sup>67</sup> , Copyright 2020 American Chemical Society). Blue and green overlay indicate topography and chemistry modifications, respectively.
35 36 37 38	650	Fang et al developed SLIPS with a one-step alcohol-assisted femtosecond laser irradiation that is
39 40 41	651	able to create porous micro/nanostructures on different substrates: stainless steel, nickel, glass and
42 43 44	652	polymer. <sup>68</sup> Fluoroalkylsilane modification was then carried out to reach superhydrophobic and
45 46 47 48	653	oleophilic surfaces. Indeed, this surface coating modified the WCA from 13° on porous stainless
49 50 51	654	steel, up to 143°. After silicon oil infusion onto the hydrophobic surface, the adhesion properties
52 53 54 55 56 57	655	were further modified, showing much lower adhesion to water droplets. This was demonstrated for
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2 3 4 5	656	various solutions with different components and viscosity: water, milk, ink, egg white, and
6 7 8	657	especially blood, which all simply slip down the tilted SLIPS. The substrates were tested in the
9 10 11 12	658	presence of green algae, a common fouling specie in marine applications. It was shown that the
13 14 15	659	combination of laser-irradiated structure and silicon oil lubricant was essential for obtaining a good
16 17 18 19	660	antibiofouling performance after seven days exposure to the green algae.
20 21 22 23	661	An antibacterial, self-cleaning and antibiofouling coating was obtained on commercial titanium
24 25 26	662	alloys, silicon, quartz and ceramic substrates. <sup>67</sup> The bottom-up process based on hot filament
27 28 29	663	chemical vapor deposition (HFCVD) allowed for the modification of complex geometries and large
30 31 32 33	664	scale substrates. A pre-seeding of the substrates was performed with detonation nanodiamond,
34 35 36	665	followed by the HFCVD process that triggered the growth of diamond hemispheres. This procedure
37 38 39	666	was repeated one time to grow an additional, smaller, diamond structure onto the first one. Finally
40 41 42 43	667	the samples were chemically modified in liquid FDTS after an oxygen plasma treatment (see Figure
44 45 46	668	10B). Antibacterial activity was evaluated against <i>P. aeruginosa</i> (MCCC1A00099) and <i>E. coli</i>
47 48 49 50	669	(ATCC 25922) by using live/dead <sup>TM</sup> staining after 24 hours incubation. These tests confirmed the
50 51 52 53	670	crucial role of the structured diamond film with <i>ca.</i> 90% and 99% reduction in bacterial adhesion
54 55 56	671	compared to untreated substrates for <i>P. aeruginosa</i> and <i>E. coli</i> , respectively. In addition, two
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672 biofouling tests with marine contaminants C. vulgaris (FACHB 44) and Ulothrix speciosa (FACHB 673 494) were conducted. Again, the structured and fluorinated samples demonstrated the best 674 antibiofouling results compared to untreated samples, but also compared to the samples modified 675 with either topography or chemistry alone. Thus it is the synergistic effect of topography and 676 surface chemistry that allows for such antibiofouling effect. 677 As a conclusion, in a vast majority, the combined topography and chemistry hydrophobic 678 approaches to produce antibiofouling surfaces lead to superhydrophobic wettability, often 679 achieving Cassie-Baxter regime. In most articles, this result is obtained only by combining 680 topography with a specific surface chemistry. The antibiofouling property thus arises from the 681 prevention adhesion mechanism cited in Figure 1. However, despite the various topography 682 designing techniques, the hydrophobic chemical entities employed are limited to either fluorine-683 based polymers or silanes, alkyl chains or infused silicon or fluorine-based oils. The next chapter 684 will demonstrate how wide the hydrophilic chemical entities library is for antibiofouling surface 685 development with combined topography and chemistry approaches. 3. Combined topography and hydrophilicity for multiple antibiofouling 686

mechanisms

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3 4 5	688	As explained in the introduction, superhydrophilic surfaces can also be used for antibiofouling
6 7 8	689	surface development. In this chapter we will focus on research articles where superwettability has
9 10 11 12	690	been achieved by combining topography and chemistry with the aim to repel biomolecules and
13 14 15	691	microorganisms. Many different techniques have been used to develop the functional topography
16 17 18	692	and deposit the chemistry of interest. All the approaches described in this chapter are detailed in
19 20 21 22	693	Table S3 of the Supporting information.
23 24 25	694	Superhydrophilic surfaces have been less explored for antibiofouling applications than
26 27 28	695	superhydrophobic one. This can explain why less common ground can be found in the literature
29 30 31	696	and why there is such a variety of solutions. In addition, as it can be seen in Figure 2, there is a
32 33 34 35	697	wide range of chemical approaches leading to hydrophilic antibiofouling surfaces. This can make
36 37 38 30	698	it challenging to find links between the various articles. However, as in the previous chapter
40 41 42	699	concerning hydrophobic approaches, three types of substrates have been studied: metals, glass and
43 44 45 46	700	polymers. This will be used to structure this part of the review, thus creating three sub-chapters.
47 48 49 50 51	701	3.1. Metallic substrates
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702	Metallic substrates are not a common material used for hydrophilic-based approaches, oppositely		
703	to hydrophobic strategies. However, these surfaces show very different characteristics,		
704	demonstrating the diversity of hydrophilic strategies for antibiofouling studies on metals.		
705	The first example of such surfaces are TiO <sub>2</sub> nanotubes coated with a Poly(ethylene) glycol (PEG)-		
706	silane, which showed different activities against fibrinogen and <i>S. aureus</i> depending on the size of		
707	the nanotubes. For this study, An and co-workers used potentiostatic anodization of Titanium to		
708	create the nanotubular effect. Two dimensions were created: nanotubes of 20 and 80 nm diameter		
709	(TN20 and TN80 respectively). This was followed by a reaction with a PEG-silane solution		
710	allowing the nanotubes to achieve better hydrophilicity (see Figure 11B). Although TN80 was more		
711	hydrophilic with a WCA of 19°, TN20 was the only surface which showed both low adhesion of		
712	model foulant fibrinogen and low friction coefficient. S. aureus was used to test the bacterial		
713	adhesion. Surprisingly, PEG-coated TN20 showed a high adhesion, similar to Ti and PEG-coated		
714	Ti, whereas all the other substrates, including PEG-coated TN80, repelled the bacteria. It seems		
715	that, depending on the size of the nanotubes, and therefore, on the available surface contact area,		
716	the antibiofouling effect can be inhibited. <sup>69</sup>		

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717	This has also been shown through the study of marine diatoms on zwitterion-coated structured
718	stainless steel substrates. Here, unlike the previous study where the topography of the initial
719	substrate was modified, an exogenous material was added to create the topography. Indeed, the
720	initial substrates were coated with aluminium through flame spray technique and micropatterned
721	with a shielding steel mesh. A layer of PDMS was then formed on the samples and allowed for
722	subsequent chemical functionalization with the zwitterionic molecule [2-(Methacryloyloxy)ethyl]-
723	dimethyl-(3-sulfopropyl)-ammonium hydroxide (pSB) through 3,4-dihydroxyphenylalanine
724	(DOPA) binding. Bovine Calf Serum proteins were used to simulate the conditioning layer
725	formation on the substrates. An antibiofouling activity was observed but was fully attributed to the
726	hydration layer brought by the pSB and the electrostatic interaction between bovine proteins and
727	dipole moment of the sulfobetaine groups. No influence of the topography was detected. The
728	antimicrobial effect of the substrates was studied with marine diatoms Cylindrotheca closterium
729	which were incubated with the samples presenting both chemical and topographical modifications,
730	in an artificial seawater-based medium. Confocal laser scanning microscopyshowed no adhesion
731	to the protuberances. However, pSB modification of reference flat samples resulted in a lower
732	density of diatoms. It is thought that the increase of the specific surface area of the patterned

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2 3 4 5	733	substrates is responsible for the higher adhesion of diatoms. A hypothesis that can be raised is that
6 7 8	734	the protuberances are too big in comparison to the size of the tested micro-organisms. <sup>70</sup>
9 10 11 12	735	One last type of metallic surface that has shown promise in antibiofouling applications due to its
13 14 15	736	hydrophilicity is bioinspired self-cleaning mucus-like hierarchical ciliary bionic antifouling
16 17 18 19	737	surfaces (SMCAS). These complex surfaces made of polyamide microfibers covered with carbon
20 21 22	738	nanotubes (CNT) and poly(vinyl alcohol) (PVA) hydrogel particles, that mimic the skin of marine
23 24 25	739	species, were designed by Ren et al with electrostatic flocking technology and solution spray (see
26 27 28 29	740	Figure 11A) to impart the so-called camouflage effect to steel surfaces, making them hard to be
30 31 32	741	recognised by the various foulants. Marine bacteria Marinobacter lipolyticus SM19(T) and
33 34 35	742	microalgae Nitzchia closterium f. minutissima were used to evaluate anti-adhesion performance of
36 37 38 39	743	the SMCAS surface. After 24 hours of co-culture, SMCAS integrally suppressed the bacterial
40 41 42	744	adhesion, showing better results than model PVA/CNT hydrogel which reduced the bacterial
43 44 45	745	adhesion to 2.0 x $10^3$ cells/cm against 5.6 x $10^5$ cells/cm on silicon. The efficacy of SMCAS,
46 47 48 49	746	explained by enhanced water-retaining, was also shown upon microalgae contact for as long as 3
50 51 52	747	weeks. Concomitantly, microfibers swaying along with the flow of seawater contributed to remove
53 54 55	748	the adhered contaminants. <sup>71</sup>
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can kill bacteria as well as impede their adhesion. The following articles use an exogenous material

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53 to tune the topography. 54 For example, nisin is an antimicrobial peptide with a hydrophilic end that has been combined to 55 microstructured glass to create efficient substrates against bacteria and diatoms. This study was 66 carried out by Lou and co-workers who began by structuring glass through ion etching before 57 functionalizing with nisin. This peptide binding protocol led to strong coatings which were stable 58 in sterile artificial sea water even after 10 days. The antibiofouling activity was assessed against 59 bacteria Bacillus sp. and diatoms P. tricornutum. The quadrangle-shaped microstructure alone 70 promoted bacterial fouling as the interspaces were bigger than the cells. However, with the nisin immobilization, antibacterial effect was confirmed. Nevertheless, the synergistic effect of 71 72 microstructure and surface chemistry appeared hard to find for bacterial fouling. Against diatoms, 73 on the other hand, which are bigger than bacteria (10  $\mu$ m vs 1-2  $\mu$ m), the anti-adhesion effect of 74 the microstructure alone was stronger. With the nisin peptide treatment, an even better anti-75 adhesion effect was detected, proving the synergistic effect of the combined approach against algal 76 foulants. Also, it was shown that an increased depth of the microstructure enhanced the anti-

77 adhesion effect of both untreated and nisin-treated glass microstructures against the diatoms.<sup>72</sup>

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778	Polyacrylic acid (PAA) has also been used for its antibacterial effect. However, it has been shown
779	to have a gram-dependant efficiency. In a study by Chen et al, layer-by-layer deposition of
780	polyelectrolytes polyvinylamine (PVAm) and PAA was the chosen method for obtaining a
781	functional coating and femto-second laser pulsing was used to acquire micro and nano-patterned
782	borosilicate glass (see Figure 12B). When testing with <i>E. coli</i> K-12 and <i>S. aureus</i> 208, it was
783	confirmed that the positive charge surface enhanced bacterial collection. <i>E. coli</i> adhesion increased
784	faster than <i>S. aureus</i> owing to its higher outer-membrane charge. Live/Dead <sup>TM</sup> staining after a 4 h
785	incubation confirmed the bactericidal activity. It was suggested that the nanostructures contributed
786	more to the bactericidal effect than the microstructures. However, no damage was observed on
787	mammalian cells. <sup>73</sup>
788	The same difference of adhesion depending on the type of bacteria was demonstrated with a film
789	of poly-(acrylic acid-co-(poly(ethylene glycol)diacrylate)) (poly(AAC-co-PEGDA)). Here, the
790	hydrogel was spin-coated onto functionalized cover slips and then treated with an argon plasma to
791	develop micro-sized wrinkles. The acrylic acid was efficiently bactericidal against both S. aureus
792	and <i>E. coli</i> , and the wrinkles contributed to lowering the amount of live microorganisms. However
793	the engineered surfaces were slightly more efficient on Gram-positive S. aureus. <sup>74</sup>

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794	Liu and co-workers produced a superhydrophilic layer of Poly(sulfobetaine methacrylate)
795	(PSBMA) by sub-surface initiated atomic transfer radical polymerization (SSI-ATRP) onto a glass
796	substrate. This technique allowed for the <i>simultaneous</i> tuning of both <i>topography and chemistry</i>
797	(as described in Figure 2). Micro-sized wrinkles were obtained, with size parameters depending on
798	the reaction time. A first study reveals the performance of the PSBMA structured surface against
799	marine environment conditions <sup>75</sup> . Static antibiofouling was assessed with red algae <i>Porphyridium</i>
800	sp. and diatoms Navicula sp. for several hours. The resulting micro-organism densities were
801	reduced by two orders of magnitude for SSI-ATRP produced surfaces compared to blank surfaces.
802	Furthermore, on structured surfaces resulting densities were 4 to 6 times smaller than on
803	unstructured ones, indicating the beneficial synergistic effect of superhydrophilic surface chemistry
804	and microsized topography. Ocean field assays over 45 days were performed. According to the
805	author, the engineered surfaces better resisted the biofouling even if the available pictures seem
806	complicated to compare. The SSI-ATRP also improved the long-term stability of the polymer
807	layer. <sup>75</sup>
808	The same team used the SSI-ATRP produced PSBMA layer in another study where the adhesion
809	of different types of foulants was investigated: macromolecules (BSA, lysozyme and fibrinogen),

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810	bacteria ( <i>E. coli</i> and <i>B. subtilis</i> ) and diatoms ( <i>Chaetoceros calcitrans</i> ). <sup>76</sup> Here, a walnut-shell-like
811	microsized surface topography was obtained. It was shown that a 2 $\mu m$ PSBMA layer prevents
812	macromolecular fouling, while a 5-10 $\mu$ m thickness is more efficient against bacteria and diatoms.
813	After a longer reaction time (8 h instead of 1, 2 or 4), the regular walnut-shell-like structures
814	became irregular blocks and antibiofouling properties were lost. <sup>76</sup>
815	PSBMA was also chosen to create zwitterionic electrostatic flocking surfaces (ZEFS). Unlike the
816	two formerly mentioned articles, here the topographical and chemical modifications were reached
817	through separate steps. The topography was first obtained by depositing nylon fibers onto glass
818	substrates by electrostatic flocking. A thin film of PSBMA was then wrapped around the
819	microfibers by radical polymerization catalyzed by Fe (see Figure 12A). It was demonstrated that
820	the diatoms <i>N. closterium f. minutissima</i> adhered very little to the fibers due to the low contact area
821	caused by their morphology. Further tests were carried out using common mussel species Mytilus
822	<i>edulis</i> , capable of choosing where to attach to the surface though exploration and thread secretion.
823	On a test board composed of glass, PDMS and ZEFS, the mussels avoided the zwitterionic coated
824	fibers, and preferentially stuck to glass. <sup>77</sup>



depending on the polymers, but rather on the application they were chosen for: marine industry, water filtration, medical devices. 3.3.1.1. Marine industry In this paragraph, the articles all aim to develop strategies for the marine industry where biofouling can have a significant economic impact. Some teams use biomimetic materials, as sea species have developed complex skin, shell or leaf surfaces to repel other, smaller organisms. Interestingly, they all use PDMS as the initial substrate which is directly modified to obtain the desired topography. In the first article, PDMS films were stretched and plasma-treated to obtain a wrinkled surface. Silanization was then performed followed by surface-initiated atom transfer radical polymerization (SI-ATRP) to produce poly(ethylene glycol)methacrylate (POEGMA) or poly(3-sulfopropyl-methacrylate) potassium salt (PSPMA) brushes on the structured surface. The growth of the polymer brushes did not have an impact on the structure. Ulva zoospores and microalgae Chlorella were mixed in the same batch at different concentrations to evaluate the marine antibiofouling of the different samples. In static conditions over 7 days, the PDMS wrinkled surface was able to reduce the amount of adhered *Chlorella* more than *Ulva* since the zoospores are smaller than the wrinkled surface size. The POEGMA and PSPMA layers on flat PDMS also showed reduced cell

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854	densities. The combination of wrinkles and polymer brushes led to the smallest cell densities.
855	PSPMA-modified PDMS (both smooth and wrinkled) was more efficient than the surface modified
856	with POEGMA brushes against Ulva zoospores. However, there was no significant differences
857	between the two polymers against Chlorella. In dynamic conditions, very little biofouling from
858	Chlorella was detected: from ~240 cells/mm <sup>2</sup> on PDMS to under 20 cells/mm <sup>2</sup> on the modified
859	substrates. Finally, a sea water assay was performed for 2 months and clearly showed the superior
860	antibiofouling effect of SI-ATRP-modified wrinkled PDMS compared to wrinkled-only or bare
861	PDMS. Again, both polymer brushes showed similar antibiofouling effects. <sup>78</sup>
862	Brzozowska's team took inspiration from marine decapod crab Myomenippe hardwickii and
863	replicated its surface composed of big and small features allowing it to repel species of various
864	sizes. To enhance the antibiofouling effect, the biomimicking structure was combined with surface
865	chemistry. Two strategies were carried out: modification with zwitterionic sulfobetaine polymer
866	brushes and layer-by-layer coating of poly(isobutylene-alt-maleic anhydride) and
867	polyethyleneimine (PEI) (Figure 13A). Tests were carried out with cyprids Amphibalanus
868	amphitrite and diatoms Amphora coffeaeformis. For both species, the lowest adhesion was
869	achieved with zwitterion brushes on patterned surfaces. This article also highlights the difference

2 3 4 5	870	between <i>in vitro</i> antibiofouling experiments and tests carried out in the field where hydrodynamics
6 7 8 9	871	have a non-negligible effect. <sup>79</sup>
10 11 12	872	A similar approach consisted of mimicking the topography of algae <i>Laminaria japonica</i> by molding
13 14 15 16	873	PDMS. Layer-by-layer coatings were also applied. In this case, they were composed of sodium
17 18 19	874	alginate and (guanidine-hexamethylenediamine-Polyethyleneimine) (poly(GHPEI)) (Figure 13B).
20 21 22 23	875	Structuring and surface chemistry modification both led to better hydrophilicity in comparison to
23 24 25 26	876	bare PDMS. The most hydrophilic, with a WCA of 35°, was the (GHPEI-ALG)-coated structured
27 28 29	877	substrate. The prepared samples were tested against diatoms N. closterium and P. tricornutum.
30 31 32	878	Structured surfaces repelled diatoms better than smooth ones. However, the combination of
33 34 35 36	879	topography and chemistry gave the most effective surfaces, with a decrease in diatom density from
37 38 39	880	nearly 1200 diatoms/mm <sup>2</sup> on smooth PDMS to under 10 diatoms/mm <sup>2</sup> on the complex surface.
40 41 42 43	881	Over a period of 14 days, the developed material also inhibited diatom growth contrarily to other
44 45 46	882	materials. Antibacterial activity was also studied with <i>E. coli</i> and was evaluated to be roughly
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The first one we will concentrate on is the polyamide (PA) membrane which has been chemically and topographically modified by various teams, leading to efficient materials for water treatment without biofilm formation. Weinman and Husson for instance, structured PA membranes with nano lines and grooves by

thermal embossing, and coated them with poly(ethyleneglycol) diglycidyl ether (PEGDE) (Figure 14A). In comparison to pristine membranes, for which the flux was reduced by over 20% over a period of 2 h, the patterned membranes did not have such a negative effect on the desired application, with a maximum reduction of 8%. The PEGDE coating caused a slight flux reduction on the patterned membranes but this impact did not increase with its concentration (5 or 15 wt%). In all experiments the salt rejection remained close to the 95% specified by the manufacturer. To test the antibiofouling capacity of these membranes, sodium alginate was used as a model foulant. It was demonstrated, by quantifying the flux over time, that both the patterning and the chemical coating decreased the fouling on the membranes. The combination of both surface hydrophilicity and improved hydrodynamics induced by the lines and grooves, gave the best results.<sup>81</sup> Choi's team, who had previously studied antibiofouling techniques based on cylindrical  $TiO_2$ 

914	membranes to shark skin inspired topography, namely Sharklet <sup>™</sup> . They reached thin film composite
915	microstructured membranes using a series of steps including phase separation micromolding and
916	layered interfacial polymerization.83-85 The structure was then combined with coating of
917	hydrophilic tannic acid, deposited from the liquid-phase, giving the membrane an anti-adhesif
918	effect (Figure 14B). <sup>85</sup> Study of the modified membranes revealed NaCl rejection and permeability
919	towards water were very similar between uncoated and coated membranes. In fact, the water
920	permeance was slightly improved due to the hydrophilicity of the coatings. As with the nanopillar
921	arrays from their previous study, <sup>82</sup> the sharkskin nanostructure coupled with a chemical coating of
922	tannic acid led to a decrease in <i>P. aeruginosa</i> attachment, shown qualitatively by live/dead <sup>TM</sup>
923	imaging. In dynamic conditions, an isolated vortex is created by the Sharkskin protrusions,
924	decreasing furthermore the ability of <i>P. aeruginosa</i> to adhere to any surface <sup>84</sup> . In their publication
925	from January 2022, Zhao et al. also used tannic acid on nanofiltration membranes for its
926	antibiofouling effect. They deposited it on a polyacrylonitrile membrane modified with
927	Glutaraldehyde (GA)-crosslinked PEI-SBMA to give it a microstructure which was tuned by
928	varying the concentrations of GA. <sup>86</sup>

Another material with physico-chemical properties that allow the fabrication of membranes is polysulfone (PSF). Various types of PSF membranes exist and have raised interest in the scientific community. In a first study, a Polyethersulfone (PES) membrane was coated with a mixture of cellulose nanofibrils (CNF) and PVA. This treatment imparted PES membranes with both nano-textured roughness and charged surface chemistry. PVA was added to crosslink the film and improve its adhesion to the substrate, decreasing the average roughness from around 30  $\mu$ m to 10  $\mu$ m. According to the author, a smaller specific surface area is expected to better prevent molecule adhesion. On the contrary of the wettability, which did not change, conserving the membrane's efficiency; the surface charge was impacted by the coating:  $\zeta$ -potential was reduced from -20 mV to -40 mV around the plateau at pH 5, indicating a higher amount of negatively charged hydroxyl and aldehyde groups. BSA adsorption on the coated membrane was evaluated using quartz crystal microbalance with dissipation monitoring (QCM-D) and was shown to be very limited. It is believed that the abundant hydrophilic groups of PVA/CNF layer suppress the interactions with the protein. A biofilm study with *E. coli* revealed that the bacterial coverage was also almost eliminated. In this case, the promising results can be explained by the combination of both surface

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

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4 5	961	biofouling. <sup>89</sup> This led to controlled pore size and an increase in water permeability and selectivity	r
7 8	962	of the membrane. The surface was also enriched with hydroxyls that increased the hydrophilicity	r
9 10 11 12	963	and decreased the biofouling of BSA.	
13 14 15	964	Finally, the last type of membrane that was found to be relevant for this review is the PVDF	7
17         18         19         20         21         22         23         24         25         26         27         28         29         30         31         32         33         34         35         36         37         38         39         40         41         42         43         44	965	membrane.	
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980	that this superwettability is only achieved by combining the two factors: the hydrophilicity of the
981	PVP coatings on the one hand, and on the other hand, the porous structure that allows the water
982	droplets to spread rapidly throughout the membrane. Antibiofouling was tested using model protein
983	BSA and fluorescently stained <i>E. coli</i> . The amount of BSA was reduced from 36 µg/cm to under
984	$2.2 \ \mu g/cm$ upon coating the PVDF membrane. This quantity was slightly increased after durability
985	tests but still remained 90% lower than adsorption on pristine membranes. However, for these
986	estimations, only the apparent surface area was studied. It is thought that the internal pores have a
987	large surface area, thus decreasing furthermore the actual protein adsorption. <sup>91</sup>
988	Furthermore, in an article by Ma and co-workers, the PVDF substrates were enhanced by
989	modification of topography and grafting of nanoparticles decorated with hydrophilic chemical
990	functions. A micro scale surface pattern was formed through imprinting with a stainless steel mesh.
991	Further nano scale topography was achieved by adding an exogenous material. Indeed, the
992	imprinted membrane was dipped into a suspension of amine-terminated $SiO_2$ nanoparticles (see
993	Figure 14C). Simultaneously, amine functions that are not involved in the surface binding thus
994	represent the new surface chemistry of the membrane. It was noted that nanoparticle
995	functionalisation alone lead to high roughness, which was wiped out when combined with micro-

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996	scale imprinting. Full wetting of water droplets observed during contact angle measurements
997	demonstrated the superhydrophilic nature of the modified membrane. Antibiofouling properties
998	were evaluated in both static conditions against bacteria suspensions ( <i>Bacillus thuringiensis</i> and <i>E</i> .
999	<i>coli)</i> at $10^8$ CFU/mL, and in dynamic conditions upon filtration tests with a practical mixed liquor
1000	sample in a full-scale aerobic membrane bioreactor. SEM analysis was used to detect the presence
1001	of bacteria. Fewer seemed to be detected on the modified membrane after rinsing, although no
1002	quantitative analysis was carried out. For the filtration tests, flux recovery measurements were
1003	performed to quantify the antibiofouling performance against the mixed liquor. The modified
1004	membrane offered a 45% higher flux recovery compared to pristine membranes, which is explained
1005	by the hydration layer arising from the superhydrophilicity, and the wave-like micro-structure that
1006	promotes turbulent flow, both reducing the adhesion of foulants to the membrane. <sup>90</sup>
1007	3.3.1.3. Medical devices
1008	Polymers are also often used in the medical field as they have many advantages in comparison to
1009	other materials. In the case of medical devices, developing strategies to stop biofilm formation on
1010	the polymeric surface is even more critical as it can often lead to nosocomial infections.

3 4 5	1011	In this study, Park et al used a cellulose acetate (CA) solution which was drop-cast on a PDMS
6 7 8	1012	master mold resulting in a flexible CA nanoneedle array. After plasma treatment, an aqueous
9 10 11 12	1013	solution of 2-methacryloryloxyethyl phosphorylcholine (MPC) was spin-coated onto the array
13 14 15	1014	before drying in a convection oven. WCA proved the superhydrophilicity of the modified CA
16 17 18	1015	surface, with angles decreasing from 70° to 9°. Antibiofouling properties were evaluated against $E$ .
19 20 21 22	1016	<i>coli</i> and <i>B. subtilis</i> suspensions in which they were incubated for 3 to 30 hours before live/dead <sup>TM</sup>
23 24 25	1017	staining for fluorescence microscopy observations. Quantitative assays were also performed to
26 27 28	1018	confirm the antibacterial effect of the optically transparent substrates. The decrease of the density
29 30 31 32	1019	of detectable bacteria in fluorescence microscopy was mainly attributed to the chemical
33 34 35	1020	modification with MPC, while the live/dead <sup>™</sup> staining assay confirmed that the nanoneedles were
36 37 38	1021	responsible for the bactericidal effect, by penetrating or stretching the bacterial membrane. <sup>92</sup> The
39 40 41	1022	same team also modified poly(ethylene glycol) dimethacrylate (PEGDMA) nanoneedles which
42 43 44 45	1023	swell in wet conditions. Interestingly, they maintained their shape upon swelling, and similarly to
46 47 48	1024	the CA nanoneedles, the best antibiofouling effect was obtained for the sample that combined the
49 50 51	1025	chemical surface modification and the presence of nanoneedle topography. With the intrinsic
53 54 55	1026	antibiofouling properties of PEGMA, MPC-PEGMA nanoneedle hybrids proved to be tough
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3 4 5	1027	antibiofouling surfaces as a local destruction of the topography or zwitterionic MPC coating was
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6 7 8 9	1028	not sufficient to totally impede the antiadhesive properties of the substrates. <sup>93</sup>
10 11 12 13	1029	Intraocular lenses have also been modified to avoid bacterial infection and minimize corneal cell
14 15 16	1030	attachment after cataract treatment. The lenses were altered by depositing a polymeric nanopillar
17 18 19	1031	array covered with ionic antibacterial polymer. The nanopillar array was produced by stamping a
20 21 22 23	1032	mix of polyurethane (PU) and Norland Optical Adhesive 63 polymer (PU/NOA63), onto a mold
24 25 26	1033	designed by photolithography. Then, iCVD was used to deposit a 50 nm thick layer of a copolymer
27 28 29	1034	of 4-vinylbenzyl chloride and 2-(dimethylamino)ethyl methacrylate. Thus, quaternary ammonium
30 31 32 33	1035	compounds (QACs) were introduced onto the surface of nanopillars. The antibacterial efficiency
34 35 36	1036	was measured against S. aureus. The nanopillar array alone demonstrated a 50% efficiency
37 38 39	1037	compared to flat PU/NOA63 polymer film, but it is only with the copolymer deposited on top that
40 41 42 43	1038	the antibacterial efficiency rised to almost 100%, confirming a profitable synergy between surface
44 45 46	1039	topography and chemistry. Upon adhesion, bacterial cells were captured in between the nanopillars,
47 48 49	1040	causing the latter to bend. The QACs available at the surface of the nanopillars are known to
50 51 52	1041	destabilize the bacterial membrane. When the nanopillars gradually restore their upright
55 54 55 56	1042	orientation, the bacteria slide down, and their membrane suffers deformation and then rupture.
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2 3 4 5	1043	However, the engineered substrate showed biocompatibility for up to 7 days towards human
6 7 8 9	1044	corneal endothelial cells. <sup>94</sup>
10 11 12 13	1045	4. Conclusion & perspectives
14 15 16	1046	As we have seen throughout this study, biofilm is a problem encountered in many different
17 18 19 20	1047	applications, ranging from medical devices to the marine industry. With antibioresistance and
21 22 23	1048	biocide resistance on the rise, and World Health Organization urging to take action, new
24 25 26	1049	antibacterial and antibiofouling strategies need to be developed. Concern is also arising over the
27 28 29	1050	toxicity of bactericidal nanoparticles or metallic compounds, making the use of such substances
30 31 32	1051	questionable. Thus, combining other solutions such as organic polymers and topography can be an
34 35 36	1052	efficient mode of action.
37 38 39 40 41	1053	More precisely, macromolecules with hydrophobic or hydrophilic properties show great interest
42 43 44	1054	for their ability to stop bacterial adhesion, and their activity can be enhanced by coating them on
45 46 47	1055	micro or nanostructured surfaces. In addition to increasing the wettability effect of certain
48 49 50	1056	substances, some structured surfaces can cause bacterial membranes to rupture through mechanical
51 52 53 54 55	1057	deformation. Others can lead to hydrodynamic fluxes which inhibit bacterial sedimentation and
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058	thus, biofouling. Precise control over the size and shape of the used structures could enable better
1059	understanding of their effect on bacterial adhesion and could also facilitate the adaptation of the
1060	surfaces to different strains of bacteria. Some structures could have opposite and non-desired
061	effects and serve as bacterial traps. Concerning hydrophilic substances, depending on their nature,
062	bactericidal properties can also be observed. All of these mechanisms are represented in Figure 15
1063	which highlights the diversity of action of hydrophilicity-based approaches in comparison to
064	hydrophobic strategies based on the Cassie-Baxter regime.
065	As emphasized by the organisation of this review, the initial material used for creating these
1066	antibiofouling surfaces with a combined approach can be metallic, glass or a variety of polymers.
1067	The adaptability to various substrates is interesting to address the wide range of applications where
068	antibiofouling surfaces are needed.
1069	However, despite all the different solutions discovered while writing this review and summarized
1070	in Table S2 and S3, there seems to be a lack of statistical experiments. Indeed, here, independent
1071	experiments have been carried out with one combination of polymer and topography and one or
1072	two species of bacteria. This lack of systematic studies has been noticed by other teams and projects
1073	are arising. Indeed, Linklater et al have published in February 2022 a first statistical study of the



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2 3 4 5	1085	critical in some domains such as medical implants, where a risk of damaging human cells is
6 7 8	1086	unconceivable. It is also important in the marine industry to protect the natural fauna and flora. In
9 10 11	1087	this review, most of the publications using hydrophobicity to inhibit biofilm formation use fluorine-
12 13 14 15	1088	based chemicals. However, concern over the negative impacts of some fluorine-containing
16 17 18	1089	compounds could lead to an increase in fluorine-free surface development in the near future.
20 21 22 23	1090	Finally, the question of the robustness and durability of these surfaces should also be studied to
23 24 25 26	1091	verify their applicability <i>in vivo</i> . Indeed, biofilm is created rapidly but becomes stronger overtime.
27 28 29 30 31 32 33 34 35 36 37 38 39 40	1092	For a device left in a liquid medium over several months, it is very important that its efficiency
	1093	does not degrade in that time. These durability assays should also be adapted depending on the
	1094	application as the stress applied to a device could be very different.
	1095	Overall, although complimentary research still needs to be carried out to respond to the yet
41 42 43	1096	unanswered questions, combining chemistry and topography seems to be a promising strategy to
44 45 46 47	1097	reach environmentally friendly, biocompatible and antibiofouling surfaces.
48 49 50 51 52	1098	SUPPORTING INFORMATION:
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1099	Table S1 showing recent review articles on antibiofouling surfaces and overview tables (S2 & S3)
1100	summarizing the combined strategies described in this manuscript.
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1102	AUTHOR INFORMATION
1103	Corresponding Author
1104	Hippolyte Durand, hippolyte.durand@cea.fr
1105	Present Addresses
1106	CEA LETI Grenoble - DRT/DTBS, 17 avenue des martyrs, 38054, Grenoble cedex 9, France
1107	Author Contributions
1108	The manuscript was written through contributions of all authors. Miss Whiteley and Mr. Durand
1109	were in charge of the gathering and analysis of the relevant articles, and of the writing of the
1110	manuscript. Mr. Mailley participated in the reviewing process and brought insights for the
1111	manuscript structure, in addition to corrections. Mr. Nonglaton participated to the development of
1112	the manuscript structure and scope, in addition to corrections. All authors have given approval to
1113	the final version of the manuscript.
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1 2 3 4 5 6	1114	‡The	ese authors contributed equally.	
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21 22	1120	and Health of Univ Grenoble Alpes CBH-EUR-GS (ANR-17-EURE-0003)		
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