



# Electrochemical (pre)treatments to prevent biofouling

Catherine Debiemme-Chouvy, Hubert Cachet

## ► To cite this version:

Catherine Debiemme-Chouvy, Hubert Cachet. Electrochemical (pre)treatments to prevent biofouling. *Current Opinion in Electrochemistry*, 2018, 11, pp.48-54. 10.1016/j.coelec.2018.07.006 . hal-01983019

**HAL Id: hal-01983019**

**<https://hal.science/hal-01983019>**

Submitted on 16 Jan 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# **Electrochemical (pre)treatments to prevent biofouling**

**Catherine Debiemme-Chouvy\*, Hubert Cachet**

## **Highlights**

Electrochemically generated hypochlorite or hypobromite species as a long-term antifouling protection of sensors in marine environment.

Hydrogen gas bubble barrier layer used to prevent biofilm.

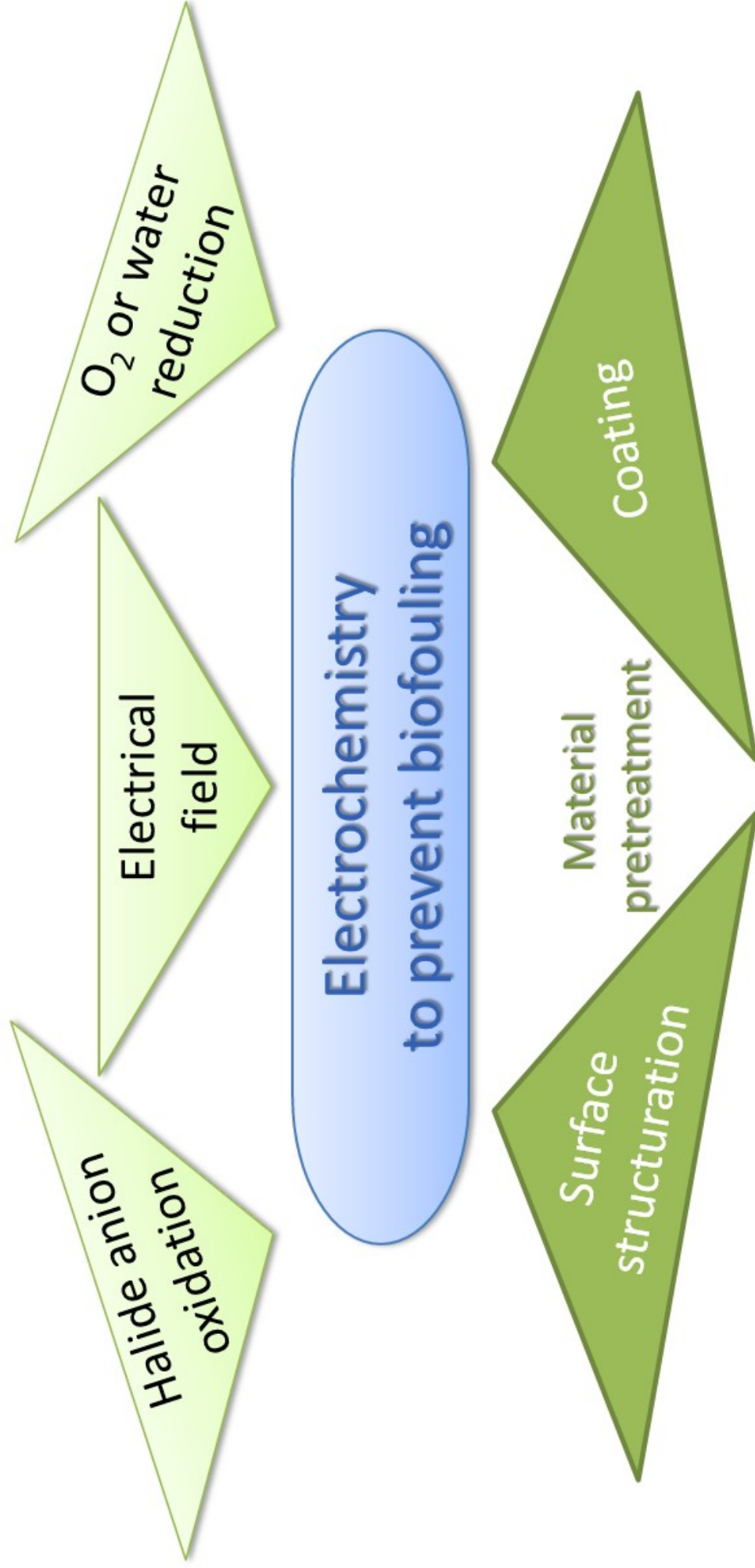
Removal of a bacterial film by vigorous evolution of hydrogen gas.

Antifouling strategy for water treatment using self-conductive or combined metal-polymer membranes.

*ac* polarization in the kHz range more efficient than *dc* cathodic or anodic one in preventing bacteria settlement.

Biocide-free antifouling method based on triboelectric conversion of mechanical energy of water wave.

Surface treatments to obtain antifouling properties: electrodeposition of coating or surface micro or nanostructuration using an electrochemical process.



# **Electrochemical (pre)treatments to prevent biofouling**

**Catherine Debiemme-Chouvy\*, Hubert Cachet**

*Laboratoire Interfaces et Systèmes Electrochimiques (LISE, UMR 8235)*

*Sorbonne Université, CNRS, 4 place Jussieu, 75005 Paris, France*

catherine.debiemme-chouvy@sorbonne-universite.fr

hubert.cachet@sorbonne-universite.fr

## **Abstract**

In order to prevent the formation of a biofilm on the surface of materials in an aqueous environment various strategies could be developed. Notably following an electrochemical route it is possible to apply a potential which could leads to (i) oxidation of halide anions leading to the formation of biocidal molecules, (ii) O<sub>2</sub> reduction leading to H<sub>2</sub>O<sub>2</sub>, (iii) water reduction leading to H<sub>2</sub> bubbles or (iv) a low-intensity electric potential. Moreover an electrochemical method could be used to nano or microstructure the material surface or to deposit on the material a coating which would avoid protein adsorption or microorganism attachment and therefore the formation of a biofilm, this coating could be an inorganic or an organic film.

**Keywords** biofouling, electrochemistry, antifouling, biocide electrogeneration, antifouling surface, applied potential



## Introduction

In contact with water, any surface is subjected to be colonized by microorganisms leading to biofouling. The development of a biofilm (Figure 1) is a major problem in various domains (see Table 1): medicine, food, maritime, water distribution systems [1] with huge impacts from an economical or/and health point of view. Therefore it is of a great importance to fight against the formation of a biofilm especially since it is very difficult to totally suppress it after its development on the surface of a material. For this purpose, using an electrochemical route two strategies could be applied [2]. The first one is an active one by applying a potential or imposing a current to an electrode placed at the vicinity of the material to be protected or to the material surface itself. This imposition leads to the generation of strong oxidants by oxidation of ions present in water ( $\text{Cl}^-$ ,  $\text{Br}^-$ ) or by water reduction with the generation of  $\text{H}_2\text{O}_2$  or with gas evolution, also an electrical field could be applied in order to obtain electrostatic repulsion of the bacteria. The second strategy is to perform a pretreatment of the material in view to either immobilize on its surface a biocide agent ( $\text{Cu}$ ,  $\text{Ag}$ ,  $>\text{N-Cl}\dots$ ) which could be released or organic coating having antifouling properties or to micro or nanostructure the material surface. The recent developments on these strategies based on electrochemical process are presented in this short review.

### A1- Electrogeneration of strong oxidants

Seawater contains in average  $10^{-3}$  M of bromide and 0.5 M of chloride, its electrolysis produces hypobromous and hypochlorous acid (or hypobromite ions ( $\text{pK}_a = 8.6$ ) and hypochlorite ions ( $\text{pK}_a = 7.5$ );  $\text{HOCl}$  is known to be 100 times more reactive than  $\text{OCl}^-$  and to be a stronger disinfectant) [3, 4] at the vicinity or directly on the material to be protected, the latter could be a glass coated with a conductive transparent tin oxide film [5]. This strategy has been applied with success to oceanographic sensors by Ifremer [6]. Pt nanostructures obtained by electrodeposition were also used to generate chlorine for marine biofouling inhibition [7, 8]. A Lab on a Chip conductivity, temperature and dissolved oxygen sensor has been protected by applying an anodic potential for 200 ms at hourly intervals, leading to generation of chlorine [9]. It has been shown that  $\text{HOCl}$  has a killing efficacy against *S. epidermidis* and *P. aeruginosa* biofilms [10].

Besides, biofilm control of metal electrodes or conductive membranes by  $\text{H}_2\text{O}_2$  production under cathodic polarization is well documented in recent works [11-13].

Electrochemical protection of underwater insulating surfaces against fouling was successfully achieved by depositing a conductive organic coating, as polyaniline-polymethyl methacrylate [14] or polypyrrole [15]. Antifouling effect was essentially assigned to  $\text{H}_2\text{O}_2$  production. The same concept was differently applied to paintable graphite sol-gel composite electrodes by imposing electrochemically generated redox and pH stresses by pole changing of the electrodes in controlled sequence, with change in the pH from 2 to 12 at the surface [16]. It must be underlined that generation of such highly oxidative ( $\text{Cl}^\bullet$ ,  $\text{OH}^\bullet$ ) or reductive ( $\text{H}^\bullet$ ) species may contribute to limit the stability of the materials to be protected against biofouling.

## **A2- Protection of surface due to gas evolution**

Recently it has been shown that hydrogen bubbles could help to prevent or mitigate bacterial colonization of wetted surfaces. Notably, vigorous evolution of hydrogen gas, by polarizing a stainless steel substrate at a potential of  $-1.5 \text{ V vs Ag/AgCl}$ , was found to be effective for removal of a bacterial biofilm within seconds [17]. By this electrochemical way, bacteria and extracellular polymeric matrix were mechanically and repeatedly removed from the substrate, suggesting this technology to be applied on various conductive surfaces. An analogous strategy was applied in the field of water treatment. Knowing that fabricating and integrating conductive membranes in current water treatment systems is not an easy task, it has been proposed to apply the electrolysis concept at the spacer component of the module rather than at the membrane itself [18]. The new membrane system is composed of a carbon-coated titanium spacer attached to the surface of a polyvinylidene fluoride microfiltration membrane. The conductive spacer works as a cathode in a three-electrode electrochemical configuration.

Concerning conductive materials, an innovative electrochemical approach for effective antifouling and antimicrobial surfaces was recently proposed [19]. Through the application of negative low-voltage square wave pulses to the conductive surface, a stainless steel sheet, a sustainable solid-gas interface was created with a hydrogen gas bubble layer formed at the metal surface. This bubble layer that remains at the surface acts as a relatively dry separation barrier due to the low solubility of water in hydrogen. The latter is able to prevent almost all bacteria adhesion. Additionally, hydrogen production leads to an arid environment which contributes to kill the preadhered bacteria on the surface due to water stress. The experiment was successfully repeated with a nickel foil, opening this technique to be applied to a large variety of conductive surfaces [19].

### A3- Effect of a low-level electric potential

Recent advances in fouling prevention concern water and waste water treatment based on membrane ultrafiltration [20]. For the first time, the effect of low voltage electric field, in the *dc* and *ac* regime, on the prevention of bacterial attachment and cell inactivation was investigated in depth in the case of conductive self-supporting carbon nanotubes (CNT) membranes used for water filtration [21]. The role of the relevant parameters on attached bacteria and cell inactivation was studied: (i) the amplitude and sign of the applied *dc* voltage; (ii) the amplitude; offset and frequency of the *ac* (square pulse) voltage; (iii) the way the electrical signal is applied, either between two auxiliary electrodes (resistive mode), or between the conductive membrane and an auxiliary electrode (capacitive mode); (iv) the flow regime, either flow-through conditions (without transmembrane pressure gradient) or cross-flow filtration (under an applied pressure). In all cases, *ac* polarization at a 1 kHz frequency is more efficient than *dc* cathodic or anodic in preventing bacteria settlement. For the first two cases, the membrane is negatively charged pushing away negatively charged bacteria, at least at low ionic strength. Cell inactivation in capacitive mode is expected to be due to direct electron transfer from bacteria leading to a decrease in their viability. Under *ac* polarization, resistive mode was found to be more efficient for antibiofouling than capacitive one, demonstrating that low current density was able to promote electrostatic and bactericidal effects sufficient to both reject and inactivate bacteria, constituting a viable strategy to hinder biofouling in water treatment systems. Such a strategy was successfully attempted to be applied to commercial polyvinylidene fluoride (PVDF) microfiltration membrane [22]. The PVDF membrane was modified by depositing interlaced carbon nanotube electrodes (ICE) allowing to impose *dc* or *ac* (10 kHz square wave) electric potentials. The combined PVDF-ICE membrane was shown to display valuable antifouling properties during filtration and backwash cycles. Regarding the interlaced electrode configuration, electrophoresis and dielectrophoresis are proposed as possible mechanisms involved in the fouling mitigation. In the same line, the application of positive or negative potentials was also studied in the case of carbonaceous electrodes for water treatment checked with a two-electrode flow cell configuration [23]. For both positive and negative applied potentials, a net decrease of biofilm development was evidenced, the larger the decrease, the larger the magnitude of the applied potential and the larger the reactive oxygen species activity. These relatively high potentials are believed to affect the redox properties of the cell membrane leading to bacterial growth inhibition.

In another work, electro-conductive carbon nanotube hollow fiber membranes were prepared as a separation material in an anaerobic bioreactor [24]. Such a membrane polarized at an optimal negative *dc* potential with respect to a titanium counter electrode was found to be efficient for reducing fouling by repulsing the negative pollutants far away from the membrane surface and yielding a lower transmembrane pressure than in the control reactor. The applied electric field is thought to offer a contending effect on forming cross-link gel layer able to give rise to an irreversible membrane fouling. An alternative route was recently proposed for protecting a PVDF membrane [25]. The membrane was embedded in a titanium mesh allowing to apply a cathodic voltage in a two-terminal configuration. The cycle of membrane fouling was extended from 60 to 98 hours. The decrease of the protein/polysaccharide ratio in sludge was thought to be the essential reason for membrane fouling mitigation.

Electrical stimulation was also employed for promoting wound healing [26]. There was evidence that *dc* cathodic currents were effective in inhibition of bacterial growth. It is thought that the main effect of such an electrical stimulation was to disrupt the bacterial membrane and to block proliferation of bacterial cells.

It is of interest to mention the first description of a biocide-free antifouling method on insulating surfaces which is enabled by electrical potential arising from the triboelectric conversion of mechanical energy of water wave [27]. Very high transient voltages are produced disturbing the charge distribution of microorganisms and subsequently preventing their adhesion.

### **B1- Inorganic coating deposited by an electrochemical route**

Copper and copper oxides are natural antimicrobial materials which have long been used to kill a wide range of pathogenic microorganisms [28-32]. Copper can be electrodeposited by reduction of Cu(II) ions whereas copper oxides can be deposited using an electro-assisted method by an increase of the pH at the cathode [31].

Since silver has natural antibacterial activity, numerous surfaces have been coated with it in order to prevent biofouling. Notably Ag has been deposited on commercial coconut shell activated carbon particles via pulsed electroreduction [33].

A Ni matrix-Ag nanoparticle composite coating having anti-corrosion and anti-fouling properties has been electrogenerated on copper substrate from nickel sulphate aqueous solution containing Ag nanoparticles (24 nm) [34].

Cobalt incorporated amorphous carbon-based (Co/a-C:H) film was deposited on silicon under high voltage in a methanol solution containing cobalt(II) acetylacetonate. This film that is superhydrophobic could have application in the fields of anti-fouling, anti-corrosion, self-cleaning [35].

### **B2- Organic polymeric coating formed by an electrochemistry process**

Organic polymeric coatings are mainly employed to protect the sensitive part of electrochemical (bio)sensor from non-specific protein or cell adsorption.

Hyaluronic acid (HA) is a hydrophilic and anionic polysaccharide (see Fig. 2A) which has been used to minimize the fouling due to non-specific adsorption of proteins and cells [36-44]. Notably electrodeposition of dopamine-conjugated hyaluronic acid has been performed by Lee et al. [38, 45] in order to protect bioelectrodes from fouling (Figure 2). Moreover hyaluronic acid has been used as dopant of conductive polymers such as PEDOT. The HA doped PEDOT film electrogenerated under potentiostatic conditions has a porous microstructure and exhibits good antifouling ability [43]. Lee and Schmidt have shown that electrooxidation of pyrrole monomers functionalized with HA leads to an electrode coating that minimized adhesion of cells [39].

Besides, a biocidal coating has been obtained by electrooxidation of chloride or bromide ions in the presence of proteins (bovine serum albumin, BSA). It has been shown that the hypochlorous or hypobromous acid electrogenerated reacts with some amino acid residues of the BSA molecules leading to its polymerization (via formation of intermolecular sulphonamide groups) and formation of haloamine functions ( $>N-Cl$  or  $>N-Br$ ) *i.e.* of an *N*-halamine coating [46, 47] which protects the material from the colonization of bacteria [48-52]. This process is summarized in Figure 3.

Finally, on conductive surfaces an *N*-halamine coating could be obtained by electroreduction of aminophenyl diazonium cations which forms a polymer containing amine groups which could be chlorinated using a NaOCl solution [53].

### **B3- Micro or nano-structuration of surface by an electrochemical treatment**

The micro or nanostructuration of surface materials can help to fight against biofouling. For example, to protect the surface of stainless steel, a microstructure was formed using an electrochemical etching (under galvanostatic conditions) followed by a chemical etching ( $\text{FeCl}_3$ ). A microstructure with a depth of 10  $\mu\text{m}$  was formed through the electrochemical etching process performed in an aqueous solution containing sulphuric and phosphoric acids [54].

Antifouling steel surface has also been obtained by electrodeposition of nanoporous tungsten oxide (TO) ( $\text{WO}_3 \cdot \text{H}_2\text{O}$  (tungstite)) converted to a superhydrophobic coating by surface functionalization using fluorinated alkylphosphate ester [55]. Actually rough and porous TO nano-textured films were created through square-waveform, pulsed, cathodic electroassisted deposition of TO using aerated aqueous sodium tungstate solution.

A strategy to fabricate an antifouling nanoporous NiTi/hydrogels composite through electrochemical de-alloying technique followed by *in situ* photopolymerization has recently been proposed. NiTi (150  $\mu\text{m}$  thick) was electrochemically dealloyed in 2 M  $\text{HNO}_3$  aqueous solution to produce hierarchically porous NiTi. In this case, Ni dissolved while Ti was oxidized with formation of  $\text{TiO}_2$  that allows in a second step photopolymerization of organic monomers. Thanks to the native superoleophobicity of hydrogels, the nanocomposite is able to completely repel oils and platelets showing excellent antibiofouling properties [56].

A de-alloying process was also applied to obtain a nanoporous gold layer having antifouling properties. To obtain such layer a two-step process was implied. The first step was electrodeposition of a white gold and silver alloy onto an electrode immersed in a solution composed of potassium dicyanoargentate and potassium dicyanoaurate and by applying a current density of 3.7  $\text{mA cm}^{-2}$ . Then the nanoporous gold electrode coating was fabricated through the de-alloying of the silver content in electrodeposited layer by immersing the electrode in concentrated nitric acid [57].

## **Concluding remarks**

The present review shows that the electrochemical route by imposing some electrical stress is extensively used to prevent biofilm formation in various ways. The well-established strategy

consisting of anodic ( $\text{HOCl}$ ,  $\text{OH}^\bullet$ ) or cathodic ( $\text{H}_2\text{O}_2$ ) generation of strong oxidants is applied to more and more various fields and at different scales.

Besides hydrogen bubbles generation was also used as a mechanical means to clean a surface or to create a separation barrier hindering biofilm formation. However the ageing of the material due to  $\text{H}_2$  that can diffuse inside the substrate is not studied.

Application of a low-level electrical potential without transfer reactions was investigated for the protection of ultrafiltration membranes for water treatment. Significant improvements were obtained from a practical point of view but most of these studies were hardly comparable because of being performed with a two-electrode configuration.

Electrochemically deposited inorganic coatings were classically designed to release biocide as metal species. New proposals were formulated in the case of electrochemically modified polymeric organic coatings notably for the protection of biosensors.

**Table 1:** Fields susceptible to biofouling, common examples and problems associated.  
Adapted from Ref. [58].

<b>Fields</b>	<b>Type</b>	<b>Problems</b>
Marine	Ship hull	Increased fuel consumption
	Ship engine	Increased stress from extra drag
	Marine platform	Increased marine structure load/stress/fatigue
	Metal	Increased biocorrosion
	Optical sensor, camera	Derivative, failure
Industrial	Membrane	Reduced flux
	Heat exchanger	Reduced convection efficiency
	Fluid flow	Frictional loss in pipes
	Drinking water	Pathogenic microorganisms in potable water
	Fuel	Diesel fuel contamination
	Food, paper and paint	Spoilage and worker health risks
Medical	Metal-cutting fluid	Filter blockage and worker health risks
	Orthopaedic implant	Removal owing to infection
	Respirator	Ventilator-associated pneumonia
	Contact lens	Eye infection
	Catheter	Urinary tract infections
	Haemodialysis	Infectious break-outs
	Teeth/dental implant	Periodontal disease, gingivitis
	Biosensor	Failure from fibrous encapsulation



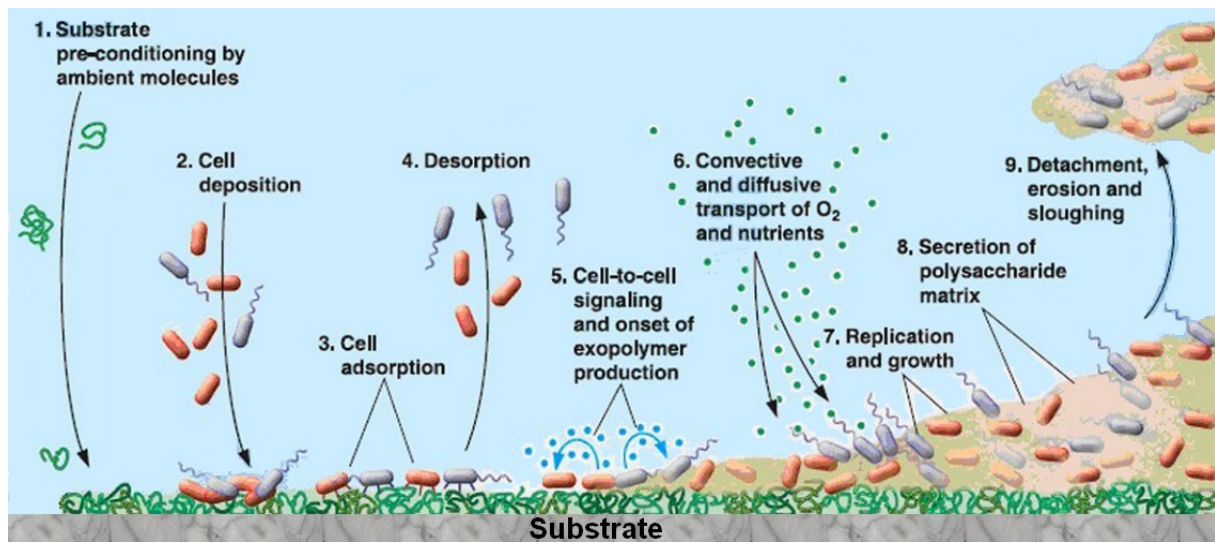


Figure 1 : The various steps of a biofilm formation and maturation.

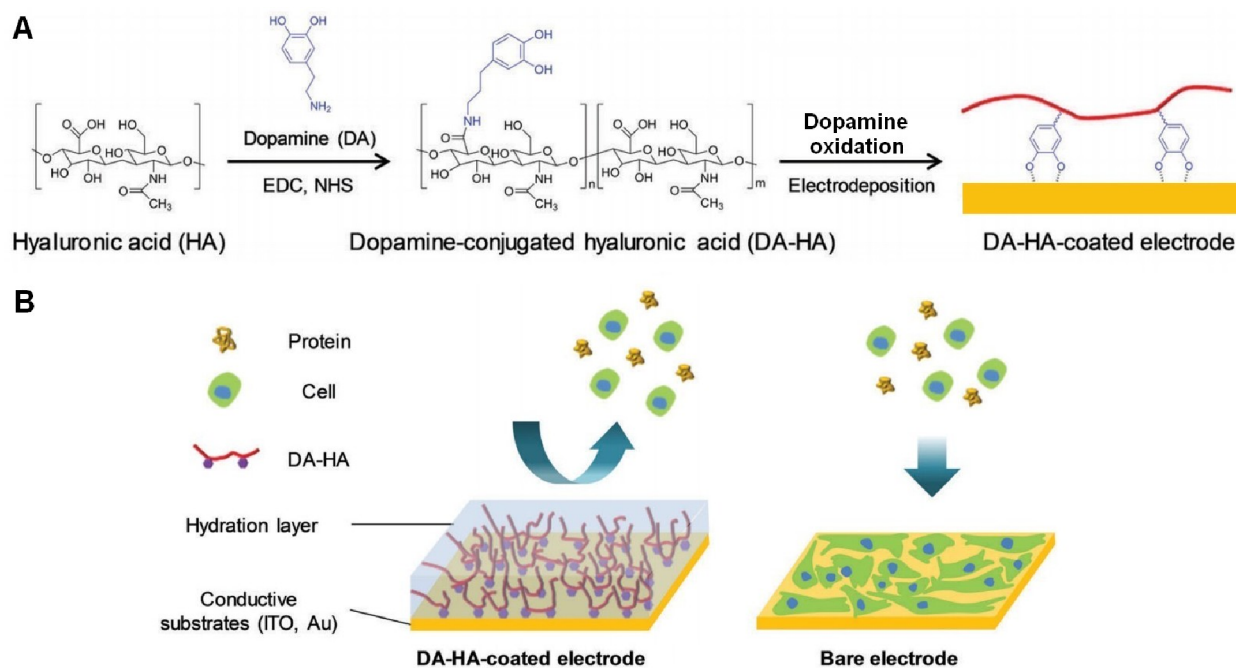
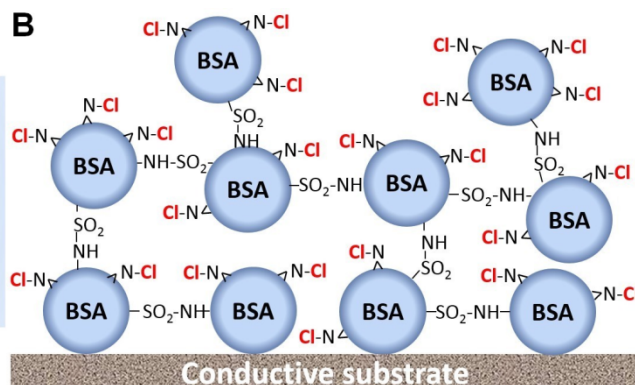


Figure 2 : A) Chemistry of dopamine conjugated hyaluronic acid (DA-HA) synthesis through amide bond formation and electrodeposition. B) Scheme illustrating the antifouling properties of the DA-HA coating. Adapted from Ref. [38].

**A**

**Chloride anodic oxidation:**  $\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{HOCl} + 2\text{e}^- + \text{H}^+$   
**Cystein side-chain oxidation:**  
 $\text{BSA-SH} + 3\text{HOCl} \Rightarrow \text{BSA-SO}_2\text{Cl} + 2\text{Cl}^- + 2\text{H}^+ + \text{H}_2\text{O}$   
**Intermolecular link:**  
 $\text{BSA-SO}_2\text{Cl} + \text{BSA-NH}_2 \Rightarrow \text{BSA-SO}_2\text{-NH-BSA} + \text{Cl}^- + \text{H}^+$   
**Chlorination:**  $\text{BSA-NH} + \text{HClO} \Rightarrow \text{BSA-NCl} + \text{H}_2\text{O}$

**B**



**Figure 3 :** A) Reactions taking place at an electrode anodically polarized in an aqueous medium containing chloride ions and BSA molecules. B) Scheme of the resulting 3D N-halamine antibacterial coating formed onto the electrode.

## References

- [1] F.G. Meng, S.Q. Zhang, Y. Oh, Z.B. Zhou, H.S. Shin, S.R. Chae, Fouling in membrane bioreactors: An updated review, *Water Research*, 114 (2017) 151-180.
- [2] S.T. Sultana, J.T. Babauta, H. Beyenal, Electrochemical biofilm control: a review, *Biofouling*, 31 (2015) 745-758.
- [3] L. Delauney, C. Compere, An Example: Biofouling Protection for Marine Environmental Sensors by Local Chlorination, in: H.C. Flemming, P.S. Murthy, R. Venkatesan, K. Cooksey (Eds.) *Marine and Industrial Biofouling 2009*, pp. 119-134.
- [4] L. Delauney, C. Compere, M. Lehaitre, Biofouling protection for marine environmental sensors, *Ocean Science*, 6 (2010) 503-511.
- [5] J.-M. Roelens, C. Nury, M. Rumeau, J. Vedel, M. Levart, *Procédé pour protéger des surfaces immergées contre les salissures et dispositif pour sa mise en œuvre.*, France, 1990.
- [6] L. Delauney, K. Boukerma, K. Bucas, J.-Y. Coail, M. Debeaumont, B. Forest, C. Garello, G. Guyader, Y. Le Bras, M. Pelleau, E. Rinnert, Biofouling protection by electro-chlorination on optical windows for oceanographic sensors and imaging devices, *OCEANS 2015 Genova*, 2015.
- [7] Z.Q. Shi, T. Wang, J. Zhao, R. Qiu, D.X. Duan, C.G. Lin, P. Wang, Pt nanostructure from electrodeposition: Electrocatalyst to generate chlorine for marine biofouling inhibition, *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 520 (2017) 522-531.
- [8] R.E. Wilson, I. Stoianov, D. O'Hare, Biofouling and in situ electrochemical cleaning of a boron-doped diamond free chlorine sensor, *Electrochemistry Communications*, 71 (2016) 79-83.
- [9] J.S. McQuillan, A.K. Morriss, M. Arundell, R. Pascal, M.C. Mowlem, The anti-bacterial effect of an electrochemical anti-fouling method intended for the protection of miniaturised oceanographic sensors, *Journal of Microbiological Methods*, 141 (2017) 63-66.
- [10] E.L. Sandvik, B.R. McLeod, A.E. Parker, P.S. Stewart, Direct Electric Current Treatment under Physiologic Saline Conditions Kills *Staphylococcus epidermidis* Biofilms via Electrolytic Generation of Hypochlorous Acid, *Plos One*, 8 (2013) e55118.
- [11] A. Ronen, W.Y. Duan, I. Wheeldon, S. Walker, D. Jassby, Microbial Attachment Inhibition through Low-Voltage Electrochemical Reactions on Electrically Conducting Membranes, *Environmental Science & Technology*, 49 (2015) 12741-12750.
- [12] O. Istanbulu, J. Babauta, H.D. Nguyen, H. Beyenal, Electrochemical biofilm control: mechanism of action, *Biofouling*, 28 (2012) 769-778.
- [13] Q.Y. Zhang, J. Nghiem, G.J. Silverberg, C.D. Vecitis, Semiquantitative Performance and Mechanism Evaluation of Carbon Nanomaterials as Cathode Coatings for Microbial Fouling Reduction, *Applied and Environmental Microbiology*, 81 (2015) 4744-4755.

- [14] M.Y. Jia, Z.M. Zhang, L.M. Yu, J. Wang, PANI-PMMA as cathodic electrode material and its application in cathodic polarization antifouling, *Electrochemistry Communications*, 84 (2017) 57-60.
- [15] M.Y. Jia, Z.M. Zhang, L.M. Yu, J. Wang, T.T. Zheng, The feasibility and application of PPy in cathodic polarization antifouling, *Colloids and Surfaces B-Biointerfaces*, 164 (2018) 247-254.
- \*[16] S. Ackermann, M. Steimecke, C. Morig, U. Spohn, M. Bron, A complementary Raman and SECM study on electrically conductive coatings based on graphite sol-gel composite electrodes for the electrochemical antifouling, *Journal of Electroanalytical Chemistry*, 795 (2017) 68-74.
- This paper presents an original study on electrochemical generation of oxidative species.*
- [17] M. Dargahi, Z. Hosseinioust, N. Tufenkji, S. Omanovic, Investigating electrochemical removal of bacterial biofilms from stainless steel substrates, *Colloids and Surfaces B-Biointerfaces*, 117 (2014) 152-157.
- [18] H.S. Abid, B.S. Lalia, P. Bertoncello, R. Hashaikh, B. Clifford, D.T. Gethin, N. Hilal, Electrically conductive spacers for self-cleaning membrane surfaces via periodic electrolysis, *Desalination*, 416 (2017) 16-23.
- \*\*[19] S.L. Gaw, S. Sarkar, S. Nir, Y. Schnell, D. Mandler, Z.C.J. Xu, P.S. Lee, M. Reches, Electrochemical Approach for Effective Antifouling and Antimicrobial Surfaces, *Acs Applied Materials & Interfaces*, 9 (2017) 26503-26509.
- Conductive surface antifouling protection by an electrochemically generated hydrogen bubble barrier layer.*
- [20] W. Zhang, L. Hau, Reactive electrochemical membrane filtration, 2017, pp. US 2017/0334751 A0334751.
- \*\*[21] C. Thamaraiselvan, A. Ronen, S. Lerman, M. Balaish, Y. Ein-Eil, C.G. Dosoretz, Low voltage electric potential as a driving force to hinder biofouling in self-supporting carbon nanotube membranes, *Water Research*, 129 (2018) 143-153.
- A detailed and comprehensive analysis of the effect of a low level ac or dc polarization for protecting a water filtration membrane against biofilm.*
- [22] Q.Y. Zhang, P. Arribas, E.M. Remillard, M.C. Garcia-Payo, M. Khayet, C.D. Vecitis, Interlaced CNT Electrodes for Bacterial Fouling Reduction of Microfiltration Membranes, *Environmental Science & Technology*, 51 (2017) 9176-9183.
- [23] S. Pandit, S. Shanbhag, M. Mauter, Y. Oren, M. Herzberg, Influence of Electric Fields on Biofouling of Carbonaceous Electrodes, *Environmental Science & Technology*, 51 (2017) 10022-10030.
- [24] Y. Yang, S. Qiao, R.F. Jin, J.T. Zhou, X. Quan, Fouling control mechanisms in filtrating natural organic matters by electro-enhanced carbon nanotubes hollow fiber membranes, *Journal of Membrane Science*, 553 (2018) 54-62.

- [25] A.Q. Ding, Q. Fan, R. Cheng, G.D. Sun, M.J. Zhang, D.L. Wu, Impacts of applied voltage on microbial electrolysis cell-anaerobic membrane bioreactor (MEC-AnMBR) and its membrane fouling mitigation mechanism, *Chemical Engineering Journal*, 333 (2018) 630-635.
- [26] M.R. Asadi, G. Torkaman, Bacterial Inhibition by Electrical Stimulation, *Advances in Wound Care*, 3 (2014) 91-97.
- \*[27] X.J. Zhao, J.J. Tian, S.Y. Kuang, H. Ouyang, L. Yan, Z.L. Wang, Z. Li, G. Zhu, Biocide-Free Antifouling on Insulating Surface by Wave-Driven Triboelectrification-Induced Potential Oscillation, *Advanced Materials Interfaces*, 3 (2016) 1600187.
- A self-powered and biocide-free antifouling method based on triboelectric conversion of mechanical energy of water motion.*
- [28] M. Hans, A. Erbe, S. Mathews, Y. Chen, M. Solioz, F. Mucklich, Role of Copper Oxides in Contact Killing of Bacteria, *Langmuir*, 29 (2013) 16160-16166.
- [29] M. Cloutier, D. Mantovani, F. Rosei, Antibacterial Coatings: Challenges, Perspectives, and Opportunities, *Trends in Biotechnology*, 33 (2015) 637-652.
- [30] F. Nishino, M. Jeem, L.H. Zhang, K. Okamoto, S. Okabe, S. Watanabe, Formation of CuO nano-flowered surfaces via submerged photo-synthesis of crystallites and their antimicrobial activity, *Scientific Reports*, 7 (2017) 1063.
- [31] Q.B. Zhang, K.L. Zhang, D.G. Xu, G.C. Yang, H. Huang, F.D. Nie, C.M. Liu, S.H. Yang, CuO nanostructures: Synthesis, characterization, growth mechanisms, fundamental properties, and applications, *Progress in Materials Science*, 60 (2014) 208-337.
- [32] S. Cao, J.D. Wang, H.S. Chen, D.R. Chen, Progress of marine biofouling and antifouling technologies, *Chinese Science Bulletin*, 56 (2011) 598-612.
- \*[33] H. Ortiz-Ibarra, R. Torres-Vitela, S. Gomez-Salazar, N. Casillas, C.P. de Leon, F.C. Walsh, Enhancement of antibacterial efficiency at silver electrodeposited on coconut shell activated carbon by modulating pulse frequency, *Journal of Solid State Electrochemistry*, 22 (2018) 749-759.
- Important as recent study on immobilization of silver on carbon particles.*
- [34] Y. Raghupathy, K.A. Natarajan, C. Srivastava, Microstructure, electrochemical behaviour and bio-fouling of electrodeposited nickel matrix-silver nanoparticles composite coatings on copper, *Surface & Coatings Technology*, 328 (2017) 266-275.
- [35] S.G. Zhou, X.B. Zhu, Q.Q. Yan, One-step electrochemical deposition to achieve superhydrophobic cobalt incorporated amorphous carbon-based film with self-cleaning and anti-corrosion, *Surface and Interface Analysis*, 50 (2018) 290-296.
- [36] S. Bauer, M.P. Arpa-Sancet, J.A. Finlay, M.E. Callow, J.A. Callow, A. Rosenhahn, Adhesion of Marine Fouling Organisms on Hydrophilic and Amphiphilic Polysaccharides, *Langmuir*, 29 (2013) 4039-4047.

- [37] R.L. Huang, X. Liu, H.J. Ye, R.X. Su, W. Qi, L.B. Wang, Z.M. He, Conjugation of Hyaluronic Acid onto Surfaces via the Interfacial Polymerization of Dopamine to Prevent Protein Adsorption, *Langmuir*, 31 (2015) 12061-12070.
- \*[38] S. Kim, Y. Jang, L.K. Jang, S.H. Sunwoo, T.I. Kim, S.W. Cho, J.Y. Lee, Electrochemical deposition of dopamine-hyaluronic acid conjugates for anti-biofouling bioelectrodes, *Journal of Materials Chemistry B*, 5 (2017) 4507-4513.
- This paper combines the great interest of hyalunoric acid for antifouling properties and of dopamine for coating adhesion.*
- [39] J.Y. Lee, C.E. Schmidt, Pyrrole-hyaluronic acid conjugates for decreasing cell binding to metals and conducting polymers, *Acta Biomaterialia*, 6 (2010) 4396-4404.
- [40] J.Y. Lee, S. Kim, Y. Jang, Method of electrochemically modifying surface of electrode using dopamine-hyaluronic acid conjugates., US 2018/0105611A1, 2018, pp. US 2018/0105611A0105611.
- [41] X. Liu, R.L. Huang, R.X. Su, W. Qi, L.B. Wang, Z.M. He, Grafting Hyaluronic Acid onto Gold Surface to Achieve Low Protein Fouling in Surface Plasmon Resonance Biosensors, *Acs Applied Materials & Interfaces*, 6 (2014) 13034-13042.
- [42] M.H. Ramadan, J.E. Prata, O. Karacsony, G. Duner, N.R. Washburn, Reducing Protein Adsorption with Polymer-Grafted Hyaluronic Acid Coatings, *Langmuir*, 30 (2014) 7485-7495.
- [43] W. Wang, M. Cui, Z.L. Song, X.L. Luo, An antifouling electrochemical immunosensor for carcinoembryonic antigen based on hyaluronic acid doped conducting polymer PEDOT, *Rsc Advances*, 6 (2016) 88411-88416.
- [44] W. Wang, S. Jayachandran, M.R. Li, S.H. Xu, X.L. Luo, Hyaluronic acid functionalized nanostructured sensing interface for voltammetric determination of microRNA in biological media with ultra-high sensitivity and ultra-low fouling, *Microchimica Acta*, 185 (2018) UNSP 156.
- [45] J.Y. Lee, S. Kim, Y. Jang, Method of electrochemically modifying surface of electrode using dopamine-hyaluronic acid conjugates., 2018.
- [46] F. Hui, C. Debiemme-Chouvy, Antimicrobial N-halamine polymers and coatings: a review of their synthesis, characterization, and applications, *Biomacromolecules*, 14 (2013) 585-601.
- [47] A. Dong, Y.J. Wang, Y.Y. Gao, T.Y. Gao, G. Gao, Chemical Insights into Antibacterial N-Halamines, *Chemical Reviews*, 117 (2017) 4806-4862.
- [48] H. Cachet, C. Debiemme-Chouvy, Evidence by EIS of the interaction between proteins and tin oxide electrode surface, *Electrochimica Acta*, 55 (2010) 6233-6238.
- [49] C. Debiemme-Chouvy, S. Haskouri, G. Folcher, H. Cachet, An original route to immobilize an organic biocide onto a transparent tin dioxide electrode, *Langmuir*, 23 (2007) 3873-3879.

- [50] C. Debiemme-Chouvy, S. Haskouri, H. Cachet, Study by XPS of the chlorination of proteins aggregated onto tin dioxide during electrochemical production of hypochlorous acid, *Applied Surface Science*, 253 (2007) 5506-5510.
- [51] C. Debiemme-Chouvy, Y. Hua, F. Hui, D. Festy, J.L. Duval, H. Cachet, Electrochemical treatments using tin oxide anode to prevent biofouling, *Electrochimica Acta*, 121 (2014) 461-461.
- [52] S. Haskouri, H. Cachet, J.L. Duval, C. Debiemme-Chouvy, First evidence of the antibacterial property of SnO<sub>2</sub> surface electrochemically modified in the presence of bovine serum albumin and chloride ions, *Electrochemistry Communications*, 8 (2006) 1115-1118.
- [53] S. Gao, H. Cachet, C. Debiemme-Chouvy, N-halamine coatings formed via the electroreduction of in situ generated diazonium cations: toward antimicrobial surfaces, *Surface and Interface Analysis*, 48 (2016) 630-635.
- [54] B.J. Hwang, S.H. Lee, Study on micro fabricated stainless steel surface to anti-biofouling using electrochemical fabrication., *Micro and Nano Syst Lett*, 5 (2017) 16.
- [55] A.B. Tesler, P. Kim, S. Kolle, C. Howell, O. Ahanotu, J. Aizenberg, Extremely durable biofouling-resistant metallic surfaces based on electrodeposited nanoporous tungstite films on steel, *Nature Communications*, 6 (2015) 8649.
- \*\*[56] D.M. Zang, H. Yi, Z.D. Gu, L. Chen, D. Han, X.L. Guo, S.T. Wang, M.J. Liu, L. Jiang, Interfacial Engineering of Hierarchically Porous NiTi/Hydrogels Nanocomposites with Exceptional Antibiofouling Surfaces, *Advanced Materials*, 29 (2017) 1602869.
- Electrochemically designed nanoporous Ni-Ti- photopolymerized hydrogel composites exhibit superoleophobicity and excellent antifouling properties.*
- [57] S. Saraf, C.J. Neal, S. Park, S. Das, S. Barkam, H.J. Cho, S. Seal, Electrochemical study of nanoporous gold revealing anti-biofouling properties, *Rsc Advances*, 5 (2015) 46501-46508.
- [58] G.D. Bixler, B. Bhushan, Biofouling: lessons from nature, *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences*, 370 (2012) 2381-2417.