

Electrochemical (pre)treatments to prevent biofouling

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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.

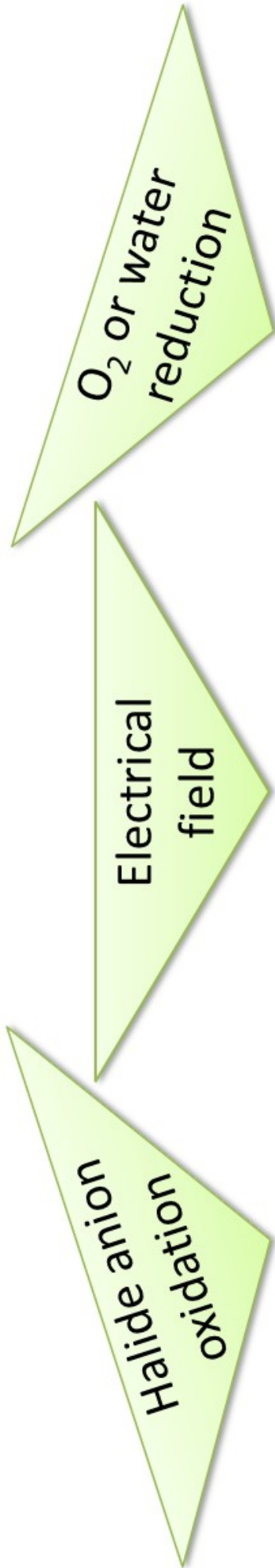
Removal of a bacterial film by vigorous evolution of hydrogen gas.

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.



**Electrochemistry
to prevent biofouling**



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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) O₂ reduction leading to H₂O₂, (iii) water reduction leading to H₂ 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 (Cl^- , Br^-) or by water reduction with the generation of H_2O_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 (Cu , 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 ($\text{pK}_a = 7.5$); HOCl is known to be 100 times more reactive than 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 HOCl has a killing efficacy against *S. epidermidis* and *P. aeruginosa* biofilms [10].

Besides, biofilm control of metal electrodes or conductive membranes by H_2O_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 H₂O₂ 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 (Cl•, OH•) or reductive (H•) 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 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 nanostructuring 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 (FeCl_3). A microstructure with a depth of 10 μm 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 μm thick) was electrochemically dealloyed in 2 M HNO_3 aqueous solution to produce hierarchically porous NiTi. In this case, Ni dissolved while Ti was oxidized with formation of 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 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 (HOCl, OH•) or cathodic (H₂O₂) 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 H₂ 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].

Fields	Type	Problems
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	

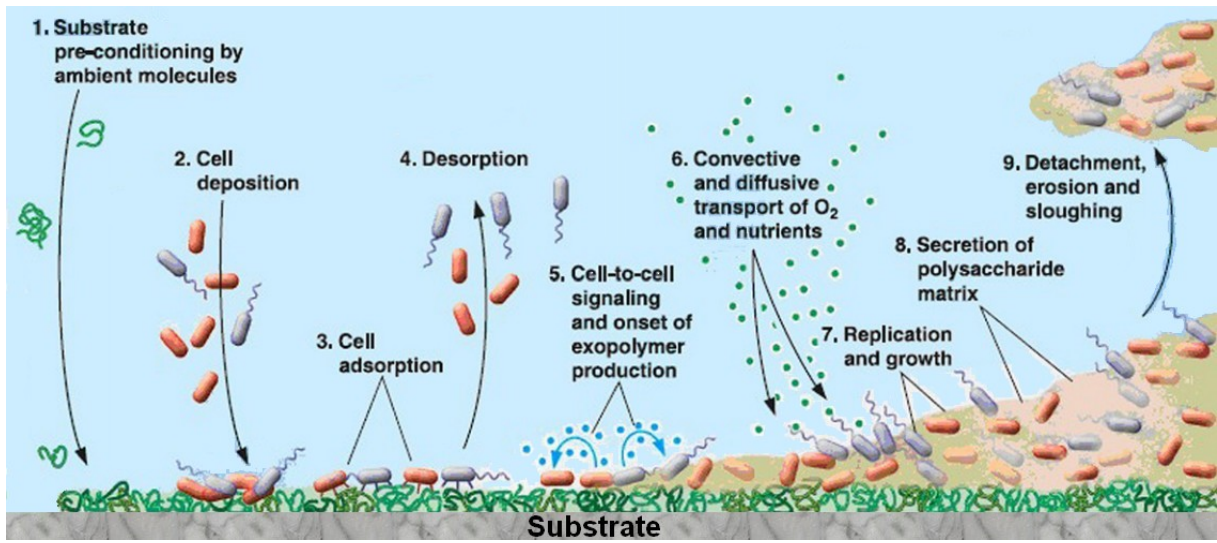


Figure 1 : The various steps of a biofilm formation and maturation.

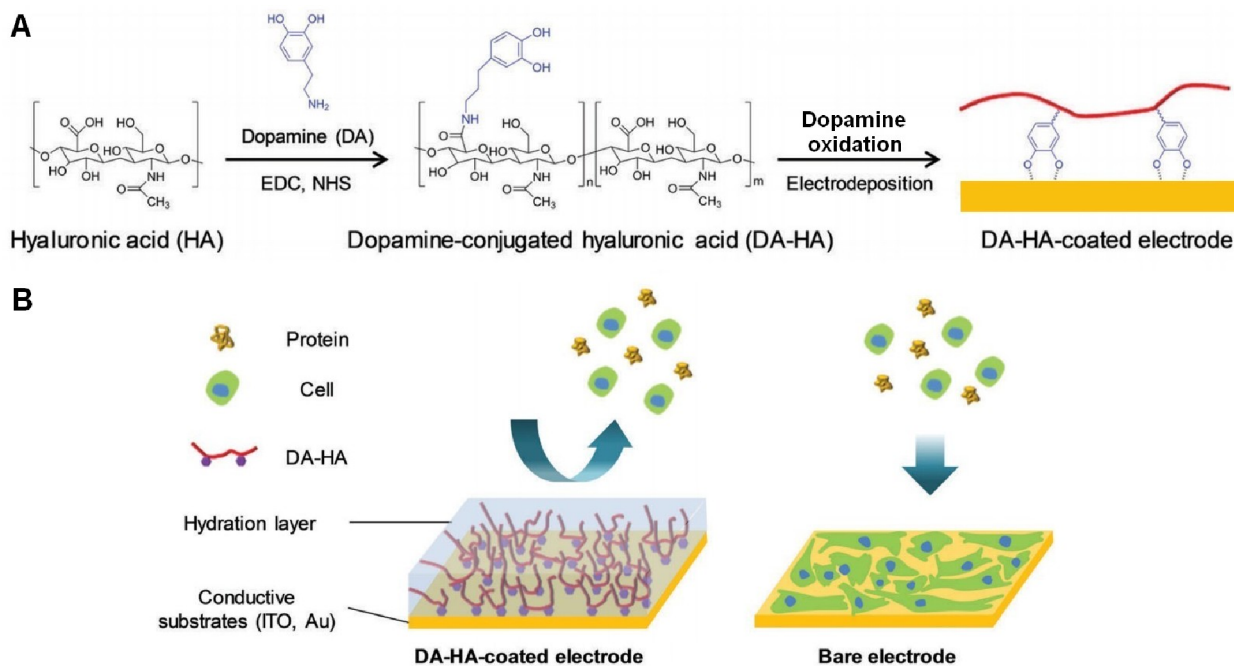
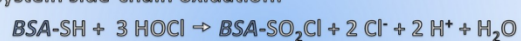


Figure 2 : A) Chemistry of dopamine conjugated hyaluronic acid (DA-HA) synthesis through amide bond formation and electrodeposition. B) Scheme illustrating the antifouling properties of the DA-HA coating. Adapted from Ref. [38].

A

Chloride anodic oxidation: $\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{HOCl} + 2 \text{e}^- + \text{H}^+$

Cystein side-chain oxidation:



Intermolecular link:



Chlorination: $\text{BSA}>\text{NH} + \text{HClO} \rightarrow \text{BSA}>\text{NCl} + \text{H}_2\text{O}$

B

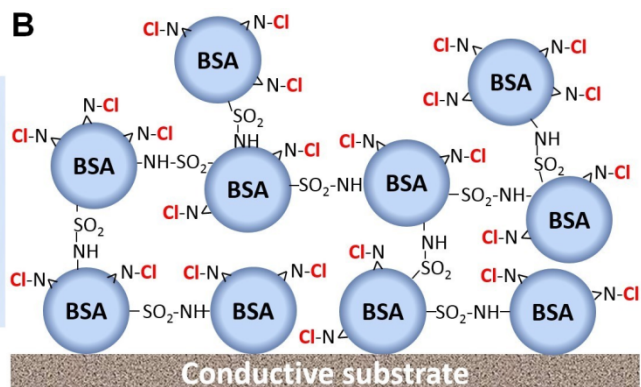


Figure 3 : A) Reactions taking place at an electrode anodically polarized in an aqueous medium containing chloride ions and BSA molecules. B) Scheme of the resulting 3D N-halamine antibacterial coating formed onto the electrode.

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