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Short review

Surface modification of materials to encourage beneficial biofilm formation

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Abstract: Biofilms are communities of sessile microorganisms that grow and produce extrapolymeric substances on an abiotic or biotic surface. Although biofilms are often associated with negative impacts, the role of beneficial biofilms is wide and include applications in bioremediation, wastewater treatment and microbial fuel cells. Microbial adhesion to a surface, which is highly dependent on the physicochemical properties of the cells and surfaces, is an essential step in biofilm formation. Surface modification therefore represents an important way to modulate microbial attachment and ultimately biofilm formation by microorganisms. In this review different surface modification processes such as organosilane surface modification, plasma treatment, and chemical modification of carbon nanotubes, electro-oxidation and covalent-immobilization with neutral red and methylene blue molecules are outlined. The effectiveness of these modifications and their industrial applications are also discussed. There is inadequate literature on surface modification as a process to enhance beneficial biofilm formation. These methods need to be safe, economically viable, scalable and environmental friendly and their potential to fulfil these criteria for many applications has yet to be determined.

Keywords: biofilms; chemical; organosilanes; modifications; plasma; surface

1. Introduction

Biofilms are a community of sessile microorganisms consisting of single or multiple strains and species that grow and form a slimy layer on an abiotic or biotic surface. This is achieved through the

production of extrapolymeric substances (EPS) and associated with an altered gene expression profile [1,2,3]. Biofilms tend to occur in moist environments with rich nutrient flow and high concentrations of cellular metabolites which enable surface attachment. Cells in biofilms are able to resist environmental stresses because they are protected within a matrix [4]. The adhesion of microbes to an abiotic surface are usually mediated by non-specific interactions whereas adhesion to a biotic surface is usually achieved through specific molecular docking mechanisms such as lectin and ligand interactions [5].

Although biofilms are often perceived to be detrimental, many biofilms are beneficial. These beneficial biofilms are associated with food fermentation, bioremediation, wastewater treatment and microbial fuel cells [3,6,7,8]. As microbial adhesion to a surface is an essential step of biofilm formation, factors affecting this adhesion such as hydrophobic interactions, electrostatic interactions, substratum surface roughness, surface charges and cell surface structures will also influence the biofilm formation on the surface [9].

Surface modification has emerged as an important approach to decrease or enhance biofilm formation. This modification entails permanently altering the properties of surfaces by chemical or physical means and consequently changing its interaction with the environment and affecting microbial attachment [10].

In this review, different types of well-established surface modification techniques such as organosilane surface modification, plasma treatments, chemical modification of carbon nanotubes, nitric acid treatment and covalent-immobilization with neutral red (or methylene blue) molecules are outlined. The effectiveness of these modifications and their industrial applications are also discussed. A summary of studies reporting surface modification involving enhancement of biofilm formation are shown in Table 1.

2. Biofilms

The biofilm matrix (or the glycocalyx) is predominantly anionic and creates an efficient scavenging system for trapping and concentrating essential minerals and nutrients for the growth of biofilms [5,11]. In addition, the glycocalyx provides a better protection against environmental threats including biocides, antibiotics, antibody, surfactants, bacteriophages and predators foraging for the cells inhabiting it as compared to planktonic cells [5,11,12,13]. It is important to understand the mechanisms of biofilm formation in order to develop effective strategies for controlling harmful biofilm formation and/or promoting beneficial biofilm formation. Surface conditioning films may be regarded as the initial step in biofilm formation [14–17]. A conditioning film on a specific surface is formed when there are sufficient nutrients, such as macromolecules and proteins, available for microbial adhesion. The adsorption of the macromolecules onto the surface alters its physicochemical properties thereby affecting bacterial adhesion [18]. Microbial attachment to a surface is an essential step in biofilm formation [19]. Primary adhesion is reversible and depends on the net sum of attractive or repulsive forces generated between the microbe and the surface [10]. These forces include hydrophobic and electrostatic interactions, van der Waals forces, hydrodynamic forces and steric hindrance [20,21,22]. The second stage of adhesion is the locking phase that is mediated by specific adhesion to the surface [20]. At this stage, loosely bound microorganisms consolidate the adhesion process by producing exopolysaccharide complexes between surfaces and receptor-specific ligands located on the pili and fimbriae depending on the characteristics of the microorganism [10].

Table 1. Surface modifications to enhance biofilm formation for beneficial use.

Modifications		Surfaces	Applications	References
Organosilanes	3-(3-amino-2-hydroxy-1-propoxy) propyldimethoxysilane	Chamotte porous surfaces	Yeast fermentation system	Berlowska et al. [6]
	3-(N-N-dimethyl-N-2-hydroxyethyl) ammonium propyldimethoxysilane	Chamotte porous surface	Yeast fermentation system	Berlowska et al. [6]
	g-aminopropyltrietoxysilane	Stainless steel	Yeast fermentation system	Bekers et al. [80]
Plasma	Oxygen plasma or nitrogen plasma	Glass, carbon felt and graphite electrode	Bioelectrochemical system	Flexer et al. [89]
	Atmospheric air plasma	Graphite and carbone felt electrode	Bioelectrochemical system	Epifano et al. [42]
	Nitrogen plasma	Carbon anode	Microbial fuel cells	He et al. [90]
	Plasma polymerization of methoxy-PEG-amine (-PEG-NH_2) and methoxy-PEG aldehyde (-PEG-CH_3)	Polyethylenimine	Wastewater treatment	Lackner et al. [8]
Conducting polymers	Polypyrrole (PPy)-carbon nanotubes (CNT)s and polyaniline (PANI)-CNTs	Carbon nanotubes anode	Microbial fuel cells	Qiao et al. [116] Zou et al. [113]
	Poly vinyl alcohol and thiophene	Carbon nanotubes electrodes	Microbial biosensors	Malhotra et al. [112]
Natural-based polymer	Chitosan	Carbon nanotubes anode	Microbial fuel cells	Nambiar et al. [117]
	Chitosan	Carbon nanotubes electrodes	Microbial biosensors	Odaci et al. [115]

Noble metals	Platinum	Carbon nanotubes anode	Microbial fuel cells	Sharma et al. [114]
Microorganisms	*Ralstonia solanacearum*	Carbon nanotubes immobilization surfaces	Bioremediation	Yan et al. [95]
	Dechlorinating bacteria	Carbon nanotubes immobilization surfaces	Bioremediation	Kanepalli & Donna [120]
	Yoghurt waste	Graphite felt	Bioelectrochemical system	Cercado-Quezada et al. [124]
Other chemicals	Sulphuric acid and heat	Graphite electrodes	Bioelectrochemical system	Tang et al. [123]
	Electrochemical oxidation (e.g. concentrated nitric acid and sulphuric acid)	Graphite electrodes	Bioelectrochemical system	Kang et al. [7]
	Ammonia gas at 700°C	Carbon cloth anode	Microbial fuel cells	Cheng & Logan [125]
	Manganese oxide	Graphite anode	Microbial fuel cells	Park & Zeikus [126]
	Nitric acid, ammonium nitrate and hydrazine hydrate	Carbon mesh	Microbial fuel cells	Zhou et al. [127] Jin et al. [128]
	Covalently immobilized neutral red (NR) and methylene blue (MB)	Carbon electrodes	Microbial fuel cells	Popov et al. [129] Guo et al. [130]

This adhesion becomes irreversible and the microbes attached firmly to the surface. The attached microbes will form aggregates on the surface. Once the microbes have irreversibly attached to surfaces, maturation of the biofilm begins to occur [10]. This process entails the enhancement of the complexity of the biofilm as the attached microbes multiply and interact with the surrounding environments which result in differential microbial growth patterns and metabolic reactions [10]. A time of approximately 10 days are needed for a biofilm to achieve structural maturity [22].

Biofilms are the source of persistent infections of many pathogenic microbes due to their high resistance to antibiotics. They are responsible for dental caries, nosocomial and other infections [23]. Biofilms are also detrimental in industries causing, for example, a reduction in efficiency of heat exchangers and cooling towers [24], decomposition of reverse osmosis membranes [25], corrosion of metal surfaces and contamination of food processing equipment [5]. However, there are several beneficial biofilms associated with bioremediation, wastewater treatment and generation of electricity in microbial fuel cells as discussed below.

2.1. Factors affecting biofilm formation on surfaces

As mentioned above, an essential step of biofilm formation is the attachment of microbial cells to surfaces. It is therefore important to understand the factors that contribute to microbial adhesion. Microbial adhesion is affected by the physicochemical properties of the substratum surfaces, cell surfaces, and the interaction between them [19,26]. Successful adhesion is achieved when hydrogen bonding, ionic and dipole interactions, electrostatic interactions, hydrophobic and hydrophilic interactions between a cell surface and an abiotic surface are strong and the distance between the cell and the surface is less than 5 mm [27]. If two surfaces are hydrophobic the repulsive force between them is decreased in an aqueous environment. Adherence of cells will occur in the hydrophobic region of a hydrophilic-hydrophobic interface on a surface [28]. Although the results of studies in this phenomenon may contradict each other, hydrophobic interactions are thought to occur between the cell surface and conditioning film, increasing microbial adhesion [29]. Adhered cells will proliferate, form EPS and establish themselves by forming a multi-layered community [27]. Variation in EPS content between biofilms depends on the microorganisms, availability of the nutrients, temperature and shear forces. EPS is made up of 50 to 90% of total carbon content comprising mostly of carbohydrates and proteins [30,31]. EPS can also contain extracellular DNA (e-DNA), glycolipids, phospholipids, humic acids, uronic acids and other extracellular components in smaller quantities [32]. These EPS biopolymers are well hydrated and result in maintainance of the biofilm, increased bacterial cell surface hydrophobicity and increased bacterial adhesion. The e-DNA present in EPS has its origin from membrane vesicles or remnants of lysed cells [33]. Wastewater biofilms have been reported to contain high levels of e-DNA [33]. Recent studies have found e-DNA in the EPS of *Pseudomonas aeruginosa*, *Bacillus cereus*, *Staphylococcus epidermidis*, *Staphylococcus aureus, Streptococcus mutans, Listeria monocytogenes* and *Enterococcus faecalis* [33–38]. The e-DNA confers a negative charge that aids in the antibiotic resistance of the biofilm by sequestering cationic antibiotics [32]. There is a lack of detailed information on EPS composition for many bacterial species and strains as it varies between biofilms and analytical methods used for extraction purposes.

The wettability of a surface describes the affinity of a liquid towards a solid substrate or an interaction between a fluid and solid surface [39]. Studies have reported organic materials in a conditioning film changes the wettability and surface charge of the native surface [40]. Wettability can either create a more hydrophobic or hydrophilic environment for biofilms. Some studies have

shown that wettability of a surface increases when its native surface is modified. This is thought to cause a decrease in bacterial adhesion and EPS production, although other studies have reported that this may not be the case [41,42].

Surface roughness and/or topography is suggested to have an effect on cellular attachment and was found to influence the surface interactions between a particle and substratum surface at a short separation distances [43,44]. Irregularities such as scratches and pores on a surface increase its surface area which favours microbial adhesion and biofilm deposition [45]. Previous studies suggested that surface roughness has no correlation with adhesion [46] while other studies have reported the contrary [47,48]. The definition of surface roughness in these studies rely on subjective assessment as to what roughness is and this has resulted in the differences in results between these studies. The structures of a surface including joints, corners and welding also affect the ability of biofilm formation [49]. The ability to predict microbial attachment based on physicochemical properties is challenging due to the impact of a weak interaction which can be masked by that of stronger ones or when surface roughness is involved [9].

Biofilms express different phenotypes to planktonic cells as the cell wall structures differ in a liquid media and on a solid surface. This is due to features such as the presence of excessive carboxyl and phosphate groups on the cell surface, ionic strength of the liquid medium and the substratum surface charge, all of which contribute to the electrostatic interactions on the surface [19,50]. This also means that the surrounding environment influences the expression of cell proteins and the ability of cells to attach to a particular surface. Osmolarity of a surface affects biofilm formation as some biofilms cannot survive on a surface with medium or high osmolarity ranging from 2 to 3% sodium chloride [51]. Hydrodynamic conditions affect the metabolic activity of biofilms by altering their structure, affecting EPS production and changing biofilm thickness [24,52,53]. Biofilms formed under higher detachment forces tend to produce more extrapolysaccharides to stabilize the biofilm structure and to withstand the shear force [54,55]. Integration of all these factors ultimately enhances the pattern of microbial biofilm development.

In addition to these physicochemical factors the biological properties of the cell also play an important role. Cell surface structures such as capsules, flagella, fimbriae and pili mediate microbial adhesions and assist in the formation of biofilm and the motility of microbes [27,43].

2.2. Beneficial biofilms in bioremediation

Bioremediation is a process in which microorganisms restore the contaminated environment, such as contaminated soil and oil spills, to its original state by converting toxic, persistent and recalcitrant pollutants into non-toxic end products [3]. Common microorganisms that are capable of degrading oil are *Pseudomonas, Flavobacterium, Arthrobacter, Azotobacter, Rhodococcus* and *Bacillus* [56]. Bioremediation is more effective when facilitated by biofilm associated than planktonic cells of microbes. This is because biofilms offer increased bioavailability and faster degradation of the pollutant, resistance to toxic conditions, and accelerated use of xenobiotics [57]. In addition, the lipopolysaccharides and EPS in biofilms can serve as metal chelators which assist in the remediation of toxic contaminants such as chlorinated organics [58]. It is therefore important for surfaces and materials that facilitate a high degree of microbial colonization to be used in bioremediation process. Currently, activated carbon surfaces are widely used in bioremediation due to its highly porous structure which enables easy colonization by microbes. These surfaces also provide a modulating effect by adsorbing high concentrations of the toxicant from the bulk while regulating its availability to the attached microbes [59]. Research seeking to develop better surfaces

for large-scale bioremediation applications is underway.

2.3. Beneficial biofilms in wastewater treatment

Water from the environment may contain microbiological and chemical contaminants that must be removed or inactivated by treatment for production of safe and hygienic drinking water [60]. The use of biologically active carbon (BAC) is one of the water treatment biotechnologies developed to overcome several limitations associated with the conventional water treatment process. The BAC process utilizes granular activated carbon as a water filtration media to physically remove unwanted microbes, organic and inorganic substances. As the granular activated carbon particles became exhausted, the rough porous surfaces of this carbon are amenable to microbial colonization that then grow into a biofilm [61,62]. This naturally occurring active biofilm is capable of eliminating a significant fraction of entrapped waterborne substances and contaminants in the water source [63]. Biofilms are also employed in many different reactor configurations in wastewater treatment such as trickling filters, moving bed reactors and rotating contactors [8]. Wastewater treatment uses microbial communities close carbon, nitrogen and phosphorus cycles. Surface modification is an ideal method for enhancement of microbial growth in biofilms used for wastewater treatment.

2.4. Beneficial biofilms in microbial fuel cells

Microbial fuel cells (MFCs) are bioelectrochemical systems that use biocatalysts to generate electricity from biomass [64]. The fundamental aspect that distinguishes MFCs from conventional fuel cells is the presence of biocatalyst (bacteria and algae) on the surface of anode [65]. These electrogenic microbes convert organic substances into electricity via electron transfer from the oxidation of fuel compounds to an electrode [7]. Under favourable conditions, microbes are capable of liberating electrons and protons from organic substrates. Consequently, the protons from the anode will be transferred to the cathode via the electrolyte membrane and collected by the current collector [65]. The development of an MFC is dependent on a biofilm residing on the anode surface. This biofilm has to be active, mature and dense to achieve enhanced kinetics of substrate oxidation, bioelectrochemical reactions and finally high power production [64,65]. It is important for electrodes to be suitable surfaces for beneficial biofilm formation.

3. Surface Modifications

Surface modification is defined as a modification by any means of a native surface [10] and enables the properties of the surface to be permanently altered. This may result in changes of microbial attachment and biofilm formation as compared to the native surface [10]. Surface modifications may include approaches such as coating with organosilane, plasma treatments, chemical modifications of carbon nanotubes, nitric acid treatment and covalent-immobilization with neutral red molecules and these are discussed below.

3.1. Organosilane-coated surface modification

Organosilanes are monomeric silicon-based chemicals or silanes that have at least one silicon carbon bond (Si-CH_3). These polymers are stable and non-polar, enhancing their hydrophobic effects [66]. The hydrophobic effects of surface modification using organosilanes enhance the adsorption of microbes to a range of surfaces [67]. In addition, organosilanes are environmental friendly and provide better protection against corrosion of materials [68,69,70]. There has been

enormous effort being made to use organosilane surface modification in a wide range of applications and specifically in the food industry [66,71]. It has been found to improve physical, chemical and mechanical properties of surfaces and enhance microbial adhesion. Organosilanes are well known for use in the covalent attachment of different biomolecules to various surfaces such as silica, quartz and glass [72–77]. Studies have used organosilanes on metal, plastic, glass, rubber, ceramic, polyester and polyurethane [78]. Factors affecting the nature of organosilane surface modification include concentration of surface hydroxyl groups, type of surface hydroxyl groups, hydrolytic stability of the bond formed, and the physical characteristics of the substrate [66]. The chemical structure of silane can be modified to achieve required characteristics such as a given hydrophobicity, surface charge, specific functional groups or acid base properties needed to enhance beneficial biofilm formation [78].

Adhesion of microorganisms is important in immobilized cell technology. For example, immobilized systems using yeasts, such as *Saccharomyces cerevisiae*, attached to a range of solid carriers are useful in fermentation processes. The cell surfaces of yeasts are negatively charged due to the presence of carboxyl, phosphoryl and hydroxyl groups [79]. Specific adhesion can be enhanced by chemical based modifications such as coating surfaces with silane. According to the findings of Bekers et al. [80], modification of stainless steel with aminopropyltrietoxysilane increased the positive charge and the attachment of yeast cells. Surface topography of the stainless steel varied significantly with consistent patterns on its surface when modified with aminopropyltrietoxysilane [81]. Previous studies have investigated the effect of ceramic surfaces modified with organosilanes to determine the adhesion of different industrial brewing yeast strains as shown in Table 1 [6]. The presence of 3-(3-anino-2 hydoxy-1-propoxy) and (2-hydroxyethyl) ammonium propyldimethoxysilane groups were found to increase fermentation biomass significantly. Scanning electron microscopy showed the presence of yeast in deep crevices and clusters [6]. Immobilized cells were found to achieve a better fermentation yield in comparison to the free cells [6,66]. The concentration of surface phosphate on the yeast cells and electrical properties of the cells can sometimes enable cells to flocculate. Adhesion of yeast in solid systems such as bioreactors is achieved via the physicochemical interactions between the cells, the surface and environmental conditions including ionic strength, temperature and contact time [79].

Further studies need to be conducted to establish a more detailed mechanisms of the role of silane based derivatives surface modifications for enhancement of beneficial biofilms.

3.2. Plasma-treated surface modification

Plasma is a gas which is partially ionized into charged particles, electrons and neutral molecules [82,83]. Plasma modifies the surface of metallic materials via chemical or physical processes at the atomic or molecular level [84]. Generally the plasma gasses used for this process are argon, nitrogen, oxygen, carbon dioxide and ammonia. Low temperature thermal plasma or non-thermal plasma is artificially made and its characteristics, such as temperature and composition, can be controlled [84]. Plasma polymerization is a method which is economically feasible and requires only mild reaction conditions. The benefits of using plasma for surface modification include reduction in polymer degradation, changes of surface topography and no chemical residues after treatment. Alterations in physicochemical characteristics, including surface free energy, hydrocarbon and functional hydroxyl group content, through the use of plasma have been studied [84]. In addition the use of plasma reduces surface contaminants and renders hydrophobic surfaces highly hydrophilic. Plasma treatment enhances initial microbial cell adhesion which in turn enhances biofilm

development [85]. Wettability of the substrate surface determines adhesive properties of microbial cells [84]. The formation of functional groups by plasma contributes to wettability leading to increased adhesive properties and enhanced surface energy [42]. Okajima et al. [86], for example, showed that surface functionalization by plasma of hydrophilic groups on a carbon fibre surface enhanced surface capacitance by 28% for a particular oxygen gas feed concentration. Another study conducted by Diaz-Benito and Velasco [87] showed that an atmospheric pressure plasma torch increased the surface energy and wettability of aluminium surfaces.

The use of atmospheric and oxygen plasma on carbon based, graphite and hydrocarbon electrodes have been investigated extensively. Plasma treatment on surfaces such as electrodes mediate electron transfer and increase the current flow. Previous studies of polymer surfaces showed plasma treatment resulted in higher surface energy, greater hydrophilicity (thus enhancing bacterial attachment) and electricity flow at the anodes, although there was electrostatic repulsion between cells and the anode [88]. Radio frequency oxygen and nitrogen 25W plasma pre-treatment of electrode increased the initial anodic current from mixed culture inocula and had a higher rate of bacterial adhesion on the electrode surface and higher biofilm growth in comparison with the untreated electrodes [89]. Pre-treatment with plasma is an ideal strategy to improve bacteria electrode interaction and performance of electric current. Plasma based nitrogen ion implantation has been used to modify the anode materials in a microbial fuel cell. The treated anode which had a changed surface roughness and hydrophobicity formed a thicker layer of cells which in turn enhanced biofilm formation and electricity production [90].

The use of plasma pre-treatment has been used to increase current production and the adsorption of microbially produced flavin, which can serve as catalyst for electricity production. *Shewanella loihica* is known to secrete flavin, a redox mediator which facilitates extracellular electron transfer at the biofilm interface. Plasma pre-treatment of the electrodes, however, diminishes coulombic production but enhanced the cell attachment rate [42].

Plasma induced grafting has been used to enhance nitirifying biofilm formation on membrane surfaces. Nitirification is an important process in wastewater treatment. Throughout the nitrification process bacteria have very low growth rates and efforts need to be made to enhance biofilm formation. Studies conducted used polyethylene and polypropylene modified with a combination of plasma polymerization and wet chemistry. This resulted in plasma polymerization of methoxy-PEG-amine (-PEG-NH_2) onto the polyethylenimine and methoxy-PEG aldehyde (-PEG-CH_3). -PEG-NH_2 modification on a rough polypropylene surface as well as smooth polyethylene surface had increased biofilm formation [8]. The amino group of the -PEG-NH_2 modification acts as an attractive force for bacteria such as *Nitrosomonas europea* and *Nitrobacter winogradskyi* which enhanced biofilm formation. However there were some studies that showed different results between modified and unmodified medications [91]. Biofilm accumulation has been correlated with shear resistance studies in which -PEG-NH_2 has stronger biofilms but lower biomass compared to unmodified controls. All these studies suggest that plasma surface modification has a strong potential for various beneficial biofilm applications specifically bioelectrochemical systems, wastewater treatment and microbial fuel cells in generating electricity.

3.3. Surface modification on carbon nanotubes (CNTs)

Research performed over the past few decades on various nano-materials, and particularly on carbon nanotubes (CNTs), strongly suggest their potentially usefulness for a range of applications. CNTs were first discovered by Lijima [92] and were subsequently applied in the biomedical and

electronic industries due to the excellent electrical conductivity of individual CNTs [93]. In environmental engineering, CNTs are used for various adsorbent applications, including heavy metals [94], organic compounds such as herbicides [95], chlorinated compounds [96], disinfection by-products [97], endocrine disruptors [98], biological contaminants [99], natural organic matter [100] and cyanobacterial toxins [101]. In addition, CNTs can be utilized as membrane materials in desalination [102,103]. A CNT is a hollow, concentric cylindrical structure with the walls formed by one atom thick sheet of graphene layer and has a length of several microns (100um) extendable up to a few millimeters (~ 4 mm) [104].

Bulk CNT contains "aggregated pores" that are formed due to the entanglement of multiple individual CNTs [105]. The "aggregated pores" have the dimension of a mesospore which makes the material suitable for adsorption of microorganisms [106–110]. The "aggregated pores" of CNTs consists of four sorption sites, the interior space of individual CNTs open at both ends, the interstitial space between CNTs, the groove space formed between bundles of CNTs and on the external surface of CNT bundles [95]. However, the groove openings formed between bundles of CNTs and the outside surface area of CNT bundles are the only regions that are accessible by bacteria. Desirable biofilm formation involves adsorbing and immobilizing large concentrations of bacteria and allowing them to form confluent layers. The bacterial adsorption capacity on CNTs is larger than that of other microporous adsorbent media. Upadhyayula et al. [99] established the microbial immobilization capacity of CNTs for *Bacillus subtilis* is 37 times greater than that of activated carbon in a batch adsorption study. In a similar study, bacterial species such as *E.coli* and *S. aureus* were found to have exceptionally large adsorption affinities towards CNTs [111].

The surface area and pore volume of CNTs used for bacteria immobilization can be further enhanced by surface modification. These modifications will increase the dispersion of CNTs while inducing favourable structural changes that promote biofilm formation. As the hydrophobic nature of pristine CNTs limits their practical applications recent studies have been performed to investigate blending CNTs with materials such as conducting polymers [104,112,113], noble metals [114], natural polymers and chitosan [115]. The blended mixture is known as a CNT-nanocomposite (CNT-NC). CNT-NCs have beneficial implications including higher electrical conductivity, better operational stability, ability to operate over a wide range of physicochemical conditions (e.g. at varying temperature and pH) and greater specificity as compared to pristine CNTs [65].

The non-toxic, highly conducting CNT-NCs can be applied in MFCs for improving electron transfer from microbes to the anode. Conducting polymer-based CNT-NCs, such as polypyrrole (PPy)-CNTs and polyaniline (PANI)-CNTs anodes [113,116], are practical and economically feasible for use in MFC. These conductive polymers are able to transform the CNT structure from cytotoxic to non-cytotoxic form and also able to establish a direct electron transfer from the biocatalyst [93]. This methodology overcomes the expensive and poisonous mediators which are conventionally used in microbial fuel cells. CNTs can be modified with noble metals (e.g. platinum) to generate a suite of mediators that promote bacterial-electrode interactions. Sharma et al. [114] found that the power densities obtained by using CNT-Pt electrodes were 6 times higher than that obtained with bare graphite electrodes. CNT-Pt based nanofluids was found to trap bacterial energies efficiently from both electrogenic and non-electrogenic bacteria species (e.g. *E. coli*) and was able to channel electrons to the electrodes which enhanced the overall performance of microbial fuel cells [114]. In addition, natural polymer-based CNT-NCs such as chitosan were able to reduce the cytotoxicity of CNTs resulting in enhancement of beneficial biofilm formation in microbial fuel cells [117].

CNT-NCs enhance the electrochemical response of biosensors by increasing the electron shuttle between bacterial cells and CNT-NCs electrodes. Similarly to microbial fuel cells, conducting

polymers-based CNT-NCs such as poly vinyl alcohol and thiophene [112] are capable of mediating redox reaction and enable direct electron transfer which increase power production. Naturally available biocompatible polymers such as chitosan [115] reduced the toxicity of CNT-NCs and the directly growing biofilms of bacteria on non-toxic electrodes had the power density increased [118]. CNT-NCs based sensor materials were found to exhibit better operational stability as compared to the sensors without CNT-NCs [118]. In addition, the activity of bacterial cells detected on CNT-NCs based sensors was ~ 40–50% greater than those without CNT-NCs [115,119]. It was also reported that CNT-NCs based biosensors offered selective recognition of the contaminant and selective determination of enzymatic activity [115].

Kanepalli and Donna [120] used immobilized bacteria which were capable of the dechlorination of trichloroethylene (a highly persistent groundwater pollutant) on CNTs for bioremediation purposes. When the pollutant came into contact with CNT-bacteria nanocomposite, the pollutant was absorbed by the CNTs and detoxified by the immobilized bacteria on the surface of CNTs. Yan et al. [95] reported the removal efficiencies of cyanobacterial toxins by the CNT-*Ralstonia solanacearum* nanocomposite was 20% greater than the removal efficiency by the CNTs and the bacteria alone. Both studies suggest that CNTs were useful in bioremediation technology in treating pollutants, specifically involving organic compounds that are not adsorbed easily using other microporous adsorbent media.

Although CNTs show a promising widespread application in forming beneficial biofilms, a high cost of manufacturing CNT is one of the major factors restricting its large-scale application. CNTs are considered one of the most risky materials due to their toxicological impacts on human and ecosystems. The toxic effects are attributed to the metal content of CNTs, which may not be completely removed by purification methods [121].

3.4. Other chemical surface modifications

Currently carbon-based materials such as graphite fibre brushes, graphite rods, graphite felt, graphite plates, carbon paper and carbon cloth are the most widely used anode materials due to their high electrical conductivity, strong biocompatibility and low cost in microbial fuel cells application [122]. The persistence of beneficial biofilm can be enhanced by modifying the surfaces of electrodes. Carbon-based surfaces undergo oxidation by acid soaking in concentrated sulphuric acid and combined acid-heat anode treatment to enhance power production. Tang et al. [123] established that the carboxyl functional groups were formed due to electrochemical treatment of graphite that enables electron transfer from bacteria to electrode. Micro-cavities can be created on an electrode surface via strong anodisation that has higher ionic density of the interface and electron density of the material [124]. An electrochemical pre-treatment increases the output of a microbial anode through micro-structuring of the electrode surface. This can be achieved by conditioning the graphite felt anodes with yoghurt waste which increases current densities by a factor of around 3 [124]. Electrochemical oxidation of the anode enhanced biofilm formation of sulfate reducing bacteria, *Desulfovibrio desulfuricans* and increased current production [7]. This process was facilitated by strong hydrogen or peptide bonds between the amide groups of the bacteria such as cytochrome C and the presence of carboxyl groups on the electrodes [7].

Ammonia gas (NH_3) treatment of a carbon cloth anode at 700 °C increased the surface charge of the electrode (from 0.38 to 3.99 meq m^{-2}) and the power was increased by 48% as compared to previous results using air-cathode microbial fuel cells [125]. The power density was improved due to the high adhesion rate of bacteria during reactor start-up and high efficiency in electron transfer from

bacteria to the surface of treated anode. Graphite anode surface modified using manganese oxide was shown to optimize electricity production by metal reducing bacteria, *Shewanella putrefaciens* [126]. Zhou et al. [127] reported that a carbon mesh modified by nitric acid and ammonium nitrate had power densities increased by approximately 43% and 33%, respectively, as compared to a unmodified control anode in the microbial fuel cells. A similar study conducted by Jin et al. [128] by modifying carbon mesh with nitric acid and hydrazine hydrate had power densities improved by 24% and 19% as compared to the unmodified control. These two studies suggested that the improvement in power densities was related to changes of surface functional groups and surface area which in turn increased the bacterial adhesion leading towards biofilm formation [127,128].

Covalently immobilized neutral red (NR) and methylene blue (MB) generates high electrochemical activity, increases biofilm adhesion and contributes to high power productions. Popov et al. [129] showed immobilized MB and NR molecules on electrodes by pH-driven-physico-chemical immobilization which increased the power density, voltage production and acetate removal of the microbial fuel cells. The covalently grafted NR onto carbon electrodes by spontaneous reduction of *in situ* also generated NR diazonium salts which assisted in achieving high electrochemical activity with 3.63 ± 0.36 times higher than non-modified electrode [130].

Despite all these strategies that have shown improvements over the non-treated electrodes, dangerous chemicals (flammable or explosive chemicals or extreme conditions (such as use of NH_3 at 700 °C and concentrated HNO_3) and sometimes even long, cumbersome, and multistep techniques need to be employed. Further studies need to be conducted to clarify the interactions between the microorganisms in biofilms and the electrode surfaces that will give promising results under safe and environmental friendly conditions.

4. Conclusion

Most of the interventions mentioned above have the potential to enhance beneficial biofilm formation by surface modifications. Studies investigating these surface modification techniques for enhancing beneficial biofilms are inadequate. A safe, economic and environmental friendly surface for beneficial biofilm formations is yet to be developed. It is also important to conduct studies on surface modification at an industrial scale to simulate commercial conditions prior to drawing a conclusion on the efficacy of these surface modifications.

Conflict of Interest

The authors declare no conflict of interest.

References

1. Garrett TR, Bhakoo M, Zhang Z (2008) Bacterial adhesions and biofilms on surfaces. *Prog Nat Sci* 18: 1049–1056.
2. Heydorn A, Ersboll BK, Hentzer M (2000) Experimental reproducibility in flow chamber biofilms. *Microbiology* 146: 2409–2415.
3. Singh R, Paul D, Jain RK (2006) Biofilms: implications in bioremediation. *Trends Microbiol* 14: 389–397.
4. Spector MP, Kenyon WJ (2012) Resistance and survival strategies of *Salmonella enterica* to environmental stresses. *Food Res Int* 45: 455–481.

5. Carpentier B, Cerf O (1993) Biofilms and their consequences, with particular reference to hygiene in the food industry. *J Appl Bacteriol* 75: 499–511.
6. Berlowska J, Kregiel D, Ambroziak W (2013) Enhancing adhesion of yeast brewery strains to chamotte carriers through aminosilane surface modification. *World J Microbiol Biotechnol* 29: 1307–1316.
7. Kang CS, Eaktasang N, Kwon DY, et al. (2014) Enhanced current production by *Desulfovibrio desulfuricans* biofilm in a mediator-less microbial fuel cell. *Bioresour Technol* 165: 27–30.
8. Lackner S, Holmberg M, Terada A, et al. (2009) Enhancing the formation and shear resistance of nitrifying biofilms on membranes by surface modification. *Water Res* 43: 3469–3478.
9. Wang Y, Lee SM, Dykes GA (2014) The physicochemical process of bacterial attachment to abiotic surfaces: Challenges for mechanistic studies, predictability and the development of control strategies. *Crit Rev Microbiol*. http://dx.doi.org/10.3109/1040841X.2013.866072.
10. Dunne WM (2002) Bacterial adhesion: Seen any good biofilms lately? *Clin Microbiol Rev* 15: 155–166.
11. Costerton JW, Cheng KJ, Geesey GG, et al. (1987) Bacterial biofilms in nature and disease. *Annu Rev Microbiol* 41: 435–464.
12. Costerton JW, Lewandowski Z, Caldwell DE, et al. (1995) Microbial biofilms. *Annu Rev Microbiol* 49: 711–745.
13. Elder MJ, Stapleton F, Evans E, et al. (1995) Biofilm-related infections in ophthalmology. *Eye* 9: 102–109.
14. Ofek I, Doyle RJ (2000) Bacterial adhesion to cells and tissues. London / New York: Chapman & Hall.
15. van der Aa BC, Dufrêne YF (2002) In situ characterization of bacterial extracellular polymeric substances by AFM. *Colloid Surfaces B* 23:173–182.
16. Donlan RM (2002) Biofilms: microbial life on surfaces. *Emerg Infect Dis* 8: 881–890.
17. Kanematsu H, Barry DM (2015) Conditioning films, In: Kanematsu H., Barry D.M., Eds, *Biofilm and Materials Science*, New York: Springer, 9–16.
18. Lorite GS, Rodrigues CM, de Souza AA, et al. (2011) The role of conditioning film formation and surface chemical changes on *Xylella fastidiosa* adhesion and biofilm evolution. *J Colloid Interf Sci* 359: 289–295.
19. Bos R, van der Mei HC, Busscher HJ (1999) Physico-chemistry of initial microbial adhesive interactions – its mechanisms and methods for study. *FEMS Microbiol Rev* 23: 179–230.
20. An YH, Dickinson RB, Doyle RJ (2000) Mechanisms of bacterial adhesion and pathogenesis of implant and tissue infections, In: An, Y.H., Friedman, R.J., Eds, *Handbook of bacterial adhesion: principles, methods, and applications*, New Jersey: Humana Press, 1–27.
21. Boland T, Latour RA, Sutzenberger FJ (2000) Molecular basis of bacterial adhesion, In: An, Y.H., Friedman, R.J., Eds, *Handbook of bacterial adhesion: principles, methods, and applications*, New Jersey: Humana Press, 29–41.
22. Brading MG, Jass J, Lappin-Scott HM (1995) Dynamics of bacterial biofilm formation, In: Lappin-Scott, H.M., Costerton, J.W., Eds, *Microbial biofilms*, New York: Cambridge University Press, 46–63.
23. Costerton JW, Stewart PS, Greenberg EP (1999) Bacterial biofilms: A common cause of persistent infections. *Science* 284: 1318–1322.
24. Mortensen KP, Conley SN (1994) Film fill fouling in counterflow cooling towers: Mechanisms and design. *CTI J* 15: 10–25.

25. McDonogh R, Schaule G, Flemming HC (1994) The permeability of biofouling layers on membranes. *J Membr Sci* 87: 199–217.
26. Goulter RM, Gentle IR, Dykes GA (2009) Issues in determining factors influencing bacterial attachment: A review using the attachment of *Escherichia coli* to abiotic surfaces as an example. *Lett Appl Microbiol* 49: 1–7.
27. Bazaka K, Jacob MV, Truong VK, et al. (2011) The effect of polyterpenol thin film surfaces on bacterial viability and adhesion. *Polymers* 3: 388–404.
28. Bos R, Van der Mei HC, Gold J, et al. (2000) Retention of bacteria on a substratum surface with micro-patterned hydrophobicity. *FEMS Microbiol Lett* 189: 311–315.
29. Shi X, Zhu X (2009) Biofilm formation and food safety in food industries. *Trends Food Sci Tech* 20: 407–413.
30. Christensen BE, Characklis WG (1990) Physical and chemical properties of biofilms. In: Characklis W.G., Marshall K.C., Eds, *Biofilms*, New York,Wiley, 93–130.
31. Sheng G-P, Yu H-Q, Li X-Y (2010) Extracellular polymer substances (EPS) of microbial aggregates in biological wastewater treatment systems: A review. *Biotechnology Adv* 28: 882–894.
32. Flemming H-C, Wingender J (2010) The biofilm matrix. *Nature Rev Microbiol* 8:623–633.
33. Whitchurch CB, Tolker-Nielsen T, Ragas PC, et al. (2002) Extracellular DNA required for bacterial biofilm formation. *Science* 295:1487.
34. Vilain S, Pretorius JM, Theron J, et al. (2009) DNA as an adhesion: *Bacillus cereus* requires extracellular DNA to form biofilms. *Appl Environ Microbiol* 75: 2861–2868.
35. Das T, Sharma PK, Busscher HJ, et al. (2010) Role of extracellular DNA in initial bacterial adhesion and surface aggregation. *Appl Environ Microbiol* 76: 3405–3408.
36. Das T, Sharma PK, Krom BP, et al. (2011) Role of eDNA on the adhesion forces between *Streptococcus mutans* and substratum surfaces: influence of ionic strength and substratum hydrophobicity. *Langmuir* 27: 10113–10118.
37. Harmsen M, Lappann M, Knochel S, et al (2010) Role of extracellular DNA during biofilm formation by *Listeria monocytogenes*. *Appl Environ Microbiol* 76: 2271–2279.
38. Thomas VC, Thurlow LR, Boyle D, et al (2008) Regulation of autolysis-dependent extracellular DNA release by *Enterococcus faecalis* extracellular proteases influences biofilm development. *J Bacteriol* 190: 5690–5698.
39. Polson EJ, Buckman JO, Bowen D, et al (2010) An environmental-scanning electron microscope investigation into the effect of biofilm on the wettability of quartz. *Soc Pet J* 15: 223–227.
40. Neu TR (1996) Significance of bacterial surface-active compounds in interaction of bacteria with interfaces. *Microbiol Rev* 60: 151–166.
41. Olofsson A-C, Hermansson M, Elwing H (2003) N-acetyl-L-cysteine affects growth, extracellular polysaccharide production, and bacterial biofilm formation on solid surfaces. *Appl Environ Microbiol* 69: 4814–4822.
42. Epifanio M, Inguva S, Kitching M, et al. (2015) Effects of atmospheric air plasma treatment of graphite and carbon felt electrodes on the anodic current from *Shewanella* attached cells. *Bioelectrochemistry* 106: 186–193.
43. Bhattacharjee S, Ko CH, Elimelech M (1998) DLVO interaction between rough surfaces. *Langmuir* 14: 3365–3375.
44. Czarnecki J, Warszyński P (1987) The evaluation of tangential forces due to surface in homogeneties in the particle deposition process. *Colloid Surface* 22: 197–205.

45. Scheuerman TR, Camper AK, Hamilton MA (1998) Effects of substratum topography on bacterial adhesion. *J Colloid Interface Sci* 208: 23–33.
46. Chia TWR, Goulter RM, McMeekin T, et al. (2009) Attachment of different *Salmonella* serovars to materials commonly used in a poultry processing plant. *Food Microbiol* 26: 853–859.
47. Howell D, Behrends B (2006) A review of surface roughness in antifouling coatings illustrating the importance of cutoff length. *Biofouling* 22: 401–410.
48. Scardino A J, Harvey E, De Nys R (2006) Testing attachment point theory: diatom attachment on microtextured polyimide biomimics. *Biofouling* 22: 55–60.
49. Guðbjörnsdóttir B, Einarsson H, Thorkelsson G (2005) Microbial adhesion to processing lines for fish fillets and cooked shrimp: influence of stainless steel surface finish and presence of gram-negative bacteria on the attachment of *Listeria monocytogenes*. *Food Technol Biotech* 43: 55–61.
50. Li B, Logan BE (2004). Bacterial adhesion to glass and metal-oxide surfaces. *Colloids Surface B* 36: 81–90.
51. Kristich CJ, Li YH, Cvitkovitch, DG, et al. (2004) Esp-independent biofilm formation by *Enterococcus faecalis*. *J Bacteriol* 186: 154–163.
52. Stoodley P, Cargo R, Rupp CJ. (2002) Biofilm material properties as related to shear-induced deformation and detachment phenomena. *J Ind Microbiol Biotechnol* 29: 361–367.
53. Liu YJ, Tay JH (2002) Metabolic response of biofilm to shear stress in fixed-film culture. *J Appl Microbiol* 90: 337–342.
54. Ohashi A, Harada H (2004) Adhesion strength of biofilm developed in an attached-growth reactor. *Water Sci Technol* 29: 281–288.
55. Chen MJ, Zhang Z, Bott TR (1998) Direct measurement of the adhesive strength of biofilms in pipes by micromanipulation. *Biotechnol Tech* 12: 875–880.
56. Morikawa M (2006) Beneficial biofilm formation by industrial bacteria *Bacillus subtilis* and related species. *J Biosci Bioeng* 101: 1–8.
57. Singh P, Cameotra SS (2004) Enhancement of metal bioremediation by use of microbial surfactants. *Biochem Biophys Res Commun* 317: 291–297.
58. Quereshi FM. (2005) Genetic manipulation of genes for environmental bioremediation and construction of strains with multiple environmental bioremediation properties. Karachi, Pakistan: University of Karachi.
59. Salah KA, Sheleh G, Levanon D, et al. (1996) Microbial degradation of aromatic and polyaromatic toxic compounds adsorbed on powdered activated carbon. *J Biotechnol* 51: 265–272.
60. Nishijima W, Speital G (2004) Fate of biodegradable dissolved organic carbon produced by ozonation on biological activated carbon. *Chemosphere* 56: 113–119.
61. Scholz M, Martin R (1997) Ecological equilibrium on biological active carbon. *Water Res* 31: 2959–2968.
62. Takeuchi Y, Mochidzuki K, Matsunobu N, et al. (1997) Removal of organic substances from water by ozone treatment followed by biological active carbon treatment. *Water Sci Technol* 35: 171–178.
63. Zhang S, Huck P (1996) Parameter estimation for biofilm processes in biological water treatment. *Water Res* 30: 456–464.
64. Rabaey K, Clauwaert P, Aelterman P, et al. (2005) Tubular microbial fuel cells for efficient electricity generation. *Environ Sci Technol* 39: 8077–8082.

65. Upadhyayula VKK, Gadhamshetty V (2010) Appreciating the role of carbon nanotubes composites in preventing biofouling and promoting biofilms on material surfaces in environmental engineering: A review. *Biotechnol Adv* 28: 802–816.
66. Kriegel D (2014) Advances in biofilm control for food and beverage industry using organo-silane technology: A review. *Food Control* 40: 32–40.
67. Mittal KL (2009) *Silanes coupling agents in Silanes and other coupling agents*. Netherland: Koninklijke Brill NV, 1–176.
68. Van Ooij WJ, Child T (1998) Protecting metals with silane coupling agents. *Chemtech* 28: 26–35.
69. Subramanian PR, van Ooij WJ (1999) Silane based metal pretreatments as alternatives to chromating. *Surface Eng* 15: 168–172.
70. Van Schaftinghen T, LePen C, Terryn H, et al. (2004) Investigation of the barrier properties of silanes on cold rolled steel. *Electrochimica Acta* 49: 2997–3004.
71. Materne T, de Buyl F, Witucki GL (2006) Organosilane technology in coating applications: Review and perspectives. USA: Dow Corning Corporation.
72. Carré A, Birch W, Lacarriére V (2007) Glass substrate modified with organosilanes for DNA immobilization, In: Mittal, K.L., Ed., *Silanes and other coupling agents*, Netherlands: VSP Utrecht, 1–14.
73. Li N, Ho C (2008) Photolithographic patterning of organosilane monolayer for generating large area two-dimensional B lymphocyte arrays. *Lab on a Chip* 8: 2105–2112.
74. Saal K, Tätte T, Tulp I, et al. (2006) Solegel films for DNA microarray applications. *Mater Lett* 60: 1833–1838.
75. Seo JH, Shin D, Mukundan P, et al. (2012) Attachment of hydrogel microstructures and proteins to glass via thiol-terminated silanes. *Colloids Surfaces B* 98: 1–6.
76. Shriver-Lake LC, Charles PT, Taitt CR. (2008) Immobilization of biomolecules onto silica and silica-based surfaces for use in planar array biosensors. *Methods Mol Biol* 504: 419–440.
77. Yamaguchi M, Ikeda K, Suzuki M, et al. (2011) Cell patterning using a template of microstructured organosilane layer fabricated by vacuum ultraviolet light lithography. *Langmuir* 27: 12521–12532.
78. Khramov AN, Balbyshev VN, Voevodin NN, et al. (2003) Nanostructured sol-gel derived conversion coatings based on epoxy- and amino-silanes. *Prog Org Coat* 47: 207–213.
79. White JS, Walker GM. (2011) Influence of cell surface characteristics on adhesion of *Saccharomyces cerevisiae* to the biomaterial hydroxylapatite. *Antonie van Leeuwenhoek Int J Gen Mol Microbiol* 99: 201–209.
80. Bekers M, Ventina E, Karsakevich A, et al. (1999) Attachment of yeast to modified stainless steel wire spheres growth of cells and ethanol production. *Process Biochem* 35: 523–530.
81. Karsakevich A, Ventina E, Vina I, et al. (1998) The effect of chemical treatment of stainless steel wire surface on *Zymomonas mobilis* cell attachment and product synthesis. *Acta Biotechnol* 18: 255–265.
82. Friedrich J (2012) Plasma, In: Friedrich, J. *Plasma chemistry of polymer surfaces advanced techniques for surface design*, Ed., Weinheim, Germany: Wiley-VCH Verlag GmBH & Co. KGaA, 35–53.
83. Goddard JM, Hotchkiss JH (2007) Polymer surface modification for the attachment of bioactive compounds. *Prog Polymer Sci* 32: 698–725.
84. Cha S, Park YS (2014) Plasma in dentistry. *Clin Plasma Med* 2: 4–10.

85. Xiong Z, Cao Y, Lu X, et al. (2011) Plasmas in tooth root canal. *IEEE Trans Plasma Sci* 39: 2968–2969.
86. Okajima K, Ohta K, Sudoh M (2005) Capacitance behaviour of activated carbon fibers with oxygen-plasma treatment. *Electrochim Acta* 50: 2227–2231.
87. Díaz-Benito B, Velasco F (2013) Atmospheric plasma torch treatment of aluminium: Improving wettability with silanes. *Appl Surface Sci* 287: 263–269.
88. Kamgang JO, Naitali M, Herry JM, et al. (2009) Increase in the hydrophilicity and Lewis acid-base properties of solid surfaces achieved by electric gliding discharge in humid air: Effects on bacterial adherence. *Plasma Sci Technol* 11: 187–193.
89. Flexer V, Marque M, Donose BC, et al. (2013) Plasma treatment of electrodes significantly enhances the development of anodic electrochemically active biofilms. *Electrochim Acta* 108: 566–574.
90. He YR, Xiao X, Li WW, et al. (2012) Enhanced electricity production from microbial fuel cells with plasma-modified carbon paper anode. *Phys Chem Chem Phys* 14: 9966–9971.
91. Ploux L, Beckendorff S, Nardin M, et al. (2007) Quantitative and morphological analysis of biofilm formation on self-assembled monolayers. *Colloid Surface B* 57:174–181.
92. Lijima S (1991) Helical microtubules of graphitic carbon. *Nature* 354: 56–58.
93. Baughman RH, Zakhidov AA, de Heer WA. (2002) Carbon nanotubes—the route toward applications. *Science* 297: 787–792.
94. Li YH, Di ZC, Luan ZK, et al. (2004) Removal of heavy metals from aqueous solution by carbon nanotubes: adsorption equilibrium and kinetics. *J Environ Sci (China)* 16: 208–211.
95. Yan XM, Shi BY, Lu JJ, et al. (2008) Adsorption and desorption of atrazine on carbon nanotubes. *J Colloid Interface Sci* 321: 30–38.
96. Gotovac S, Yang CM, Hattori Y, et al. (2007) Adsorption of poly aromatic hydrocarbons on single walled carbon nanotubes of different functionalities and diameters. *J Colloid Interface Sci* 314: 18–24.
97. Lu C, Chung YL, Chang KF (2005) Adsorption of trihalomethanes from water with carbon nanotubes. *Water Res* 39: 1183–1189.
98. Pan B, Lin D, Mashayekhi H, et al. (2008) Adsorption and hysteresis of bisphenol A and 17-α-ethinyl estradiol on carbon nanomaterials. *Environ Sci Technol* 2008: 15.
99. Upadhyayula VKK, Deng S, Mitchell MC, et al. (2009) Application of carbon nanotube technology for removal of contaminants in drinking water: A review. *Sci Total Environ* 408: 1–13.
100. Hyung H, Kim JH (2008) Natural organic matter (NOM) adsorption to multi walled carbon nanotubes: effect on NOM characteristics and water quality parameters. *Environ Sci Technol* 42: 4416–4421.
101. Yan H, Gong A, He H, et al. (2006) Adsorption of microcystins by carbon nanotubes. *Chemosphere* 62: 142–148.
102. Corry B (2008) Designing carbon nanotube membrane for efficient water desalination. *J Phys Chem B* 112: 1427–1434.
103. Raval HD, Gohil JM (2009) Carbon nanotube membrane for water desalination. *Int J Nucl Desal* 3: 360–368.
104. Huang S, Maynor B, Cai X, et al. (2003) Ultralong well-aligned single-walled carbon nanotube architecture on surfaces. *Adv Mater* 15: 1651–1655.

105. Agnihotri S, Mota JPB, Rostam-Abadi M, et al. (2005) Structural characterization of single walled carbon nanotube bundles by experiment and molecular simulation. *Langmuir* 21: 896–904.
106. Benny TH, Bandosz TJ, Wong SS (2008) Effect of ozonolysis on the pore structure, surface chemistry, and bundling of single walled carbon nanotubes. *J Colloid Interface Sci* 317: 375–382.
107. Chen Y, Liu C, Li F, et al. (2006) Pore structures of multi walled carbon nanotubes activated by air, CO_2 and KOH. *J Porous Mater* 13: 141–146.
108. Liao Q, Sun J, Gao L (2008) Adsorption of chlorophenols by multi walled carbon nanotubes treated with HNO_3 and NH_3. *Carbon* 46: 544–561.
109. Mauter SM, Elimelech M (2008) Environmental applications of carbon based nanomaterials. *Environ Sci Technol* 42: 5843–5859.
110. Niu JJ, Wang JN, Jiang Y, et al. (2007) An approach to carbon nanotubes with high surface area and large pore volume. *Microporous Mesoporous Mater* 100: 1–5.
111. Deng S, Upadhyayula VKK, Smith GB, et al. (2008) Adsorption equilibrium and kinetics of microorganisms on single walled carbon nanotubes. *IEEE Sens* 8: 954–962.
112. Malhotra BD, Chaubey A, Singh SP (2006) Prospects of conducting polymers in biosensors. *Anal Chim Acta* 578: 59–74.
113. Zou Y, Xiang C, Yang L, et al. (2008) A mediator less microbial fuel cell using polypyrrole coated carbon nanotubes composite as anode material. *Int J Hydrogen Energ* 33: 4856–4862.
114. Sharma T, Mohana Reddy AL, Chandra TS, et al. (2008) Development of carbon nanotubes and nanofluids based microbial fuel cell. *Int J Hydrogen Energ* 33: 6749–6754.
115. Odaci D, Timur S, Telefoncu A (2009) A microbial biosensor based on bacterial cells immobilized on chitosan matrix. *Bioelectrochemistry* 75: 77–82.
116. Qiao Y, Li CM, Bao SJ, et al. (2007) Carbon nanotube/polyaniline composite as anode material for microbial fuel cells. *J Power Sources* 170: 79–84.
117. Nambiar S, Togo CA, Limson JL (2009) Application of multi-walled carbon nanotubes to enhance anodic performance of an *Enterobacter cloacae* based fuel cell. *Afr J Biotechnol* 8: 6927–6932.
118. Chen J, Yu Z, Sun J, et al. (2008) Preparation of biofilm electrode with *Xanthomonas* sp. and carbon nanotubes and the application to rapid biochemical oxygen demand analysis in high salt condition. *Water Environ Res* 80: 699–702.
119. Timur S, Anik U, Odaci D, et al. (2007) Development of microbial biosensor based on carbon nanotube (CNT) modified electrodes. *Electrochem Commun* 9: 1810–1815.
120. Kanepalli S, Donna FE (2006) Enhancing the remediation of trichloroethane (TCE) using double-walled carbon nanotubes (DWNT): United States Geological Survey.
121. Pumera M (2007) Carbon nanotubes contain residual metal catalyst nanoparticles even after washing with nitric acid at elevated temperatures because these metal nanoparticles are sheathed by several graphene sheets. *Langmuir* 23: 6453–6458.
122. Logan BE, Hamelers B, Rozendal R, et al. (2006) Microbial fuel cells: methodology and technology. *Environ Sci Technol* 40: 5181–5192.
123. Tang X, Guo K, Li H, et al. (2011) Electrochemical treatment of graphite to enhance electron transfer from bacteria to electrodes. *Bioresour Technol* 102: 3558–3560.
124. Cercado-Quezada B, Delia ML, Bergel A (2011) Electrochemical microstructuring of graphite felt electrodes for accelerated formation of electroactive biofilms on microbial anodes. *Electrochem Commun* 13: 440–443.

125. Cheng S, Logan BE (2007) Ammonia treatment of carbon cloth anodes to enhance power generation of microbial fuel cells. *Electrochem Commun* 9: 492–496.
126. Park DH, Zeikus JG (2003) Improved fuel cell and electrode designs for producing electricity from microbial degradation. *Biotechnol Bioeng* 81: 348–355.
127. Zhou M, Chi M, Wang H, et al. (2012) A new practical method to improve the performance of microbial fuel cells. *Biochem Eng J* 60: 151–155.
128. Jin T, Luo J, Yang J, et al. (2012) Coupling of anodic and cathodic modification for increased power generation in microbial fuel cells. *J Power Sources* 219: 358–363.
129. Popov AL, Kim JR, Dinsdale RM, et al. (2012) The effect of physic-chemically immobilized methylene blue and neutral red on the anode of microbial fuel cell. *Biotechnol Bioprocess Eng* 17: 361–370.
130. Guo K, Chen X, Freguia BC, et al. (2013) Spontaneous modification of carbon surface with neutral red from its diazonium salts for bioelectrochemical systems. *Biosens Bioelectron* 47: 184–189.

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