Nanocoating Is a New Way for Biofouling Prevention

Santosh Kumar1,2, Fei Ye1, Sergey Dobretsov3,4* and Joydeep Dutta1*

1Functional Materials, Department of Applied Physics, School of Engineering Sciences, KTH Royal Institute of Technology, Stockholm, Sweden, 2Department of Food Engineering and Technology, Central Institute of Technology Kokrajhar, BTR, Assam, India, 3Department of Marine Science and Fisheries, Sultan Qaboos University, Muscat, Oman, 4Center of Excellence in Marine Biotechnology, Sultan Qaboos University, Muscat, Oman

Biofouling is a major concern to the maritime industry. Biofouling increases fuel consumption, accelerates corrosion, clogs membranes and pipes, and reduces the buoyancy of marine installations, such as ships, platforms, and nets. While traditionally marine installations are protected by toxic biocidal coatings, due to recent environmental concerns and legislation, novel nanomaterial-based anti-fouling coatings are being developed. Hybrid nanocomposites of organic-inorganic materials give a possibility to combine the characteristics of both groups of material generating opportunities to prevent biofouling. The development of bio-inspired surface designs, progress in polymer science and advances in nanotechnology is significantly contributing to the development of eco-friendly marine coatings containing photocatalytic nanomaterials. The review mainly discusses photocatalysis, antifouling activity, and formulation of coatings using metal and metal oxide nanomaterials (nanoparticles, nanowires, nanorods). Additionally, applications of nanocomposite coatings for inhibition of micro- and macro-fouling in marine environments are reviewed.

Keywords: nanocoating, antifouling, biocide, polymer, hydrogel, nanomaterial

INTRODUCTION

Biofouling is a process that any substrate in the marine environment is quickly covered by organisms. Biofouling is referred to as undesirable growth on submerged surfaces of micro- (bacteria and protists) and macro-fouling (invertebrates and algae) organisms (Wahl, 1989). Any submerged substratum is quickly covered with organic molecules and particles that can be colonized by microscopic organisms, forming biofilms (Wahl, 1989). Marine biofilms contain multiple species of bacteria, microalgae and diatoms (Salta et al., 2013). Biofilms can subsequently enhance or reduce settlement of larvae and spores of invertebrates and algae (Dobretsov et al., 2006; Dobretsov and Rittschof, 2020).

The maritime industry and naval forces across the world lose billions of US dollars due to biofouling of marine installations (Yebra et al., 2004; Schultz et al., 2010; Aghajani and Esmaeili, 2021). In order to prevent biofouling, industries apply antifouling coatings on exposed surfaces. The antifouling coatings feature in antimicrobial activity and generally prevent both micro- and macrofouling. The majority of antifouling coatings use toxic inorganic (copper) and organic biocides (isothiazolone) that leach out of the coating and kill biofouling organisms (Yebra et al., 2004). However, toxic biocides affect non-targeted marine organisms as well and accumulate in the marine environment. In 2008, the most potent antifouling agent triorganotin was banned by the International Maritime Organization (IMO) due to its adverse effects on the marine environment.
The non-toxic antifouling methods available in the market are often costly and are not as effective as traditional biocidal solutions. Thus, it is necessary to develop environmentally friendly solutions and nanotechnology-based applications can be of great help in order to do create non-toxic or low-toxic antifouling coatings.

Nanotechnology involves manipulation of materials at the nanometer scale in order to improve and obtain new properties of materials (Hornyak, 2008). Nanostructures with highly controlled and tunable properties can be synthesized by self-assembling of atoms. These nanostructures can either be zero dimensional (nanoparticles) (Grzelczak et al., 2008; Hornyak, 2008), one dimensional (nanowires) (Sugunan et al., 2006), two dimensional (thin films) (Aoki et al., 2005) or three dimensional (arrays, hierarchical structures) (Von Freymann et al., 2010). At nano-scale sizes, materials possess unique size-dependent properties that differ from their bulk, which can be exploited for diverse applications, in electronics (Lah and Zubir, 2018), medicine (Uuskovopič and Bertassoni, 2010), food (Kumar et al., 2019b), fuel (Chung and Manthiram, 2019), solar cells (Fei et al., 2012), sensors (Zhu et al., 2014), and water treatment (Baruah et al., 2012).

Nanocoatings have been used for biofouling prevention. Previous work reviewed the antifouling effects of nano- and micro-scale surface patterns which are inspired by nature (Scardino and De Nys, 2011; Bixler and Bhushan, 2012; Myan et al., 2013; Graham and Cady, 2014; Richards et al., 2020). The best example of such biomimetic antifouling coating is Sharklet™ which was inspired by the microtopography of the shark skin (Bechert et al., 2000). The C18 coatings with high levels of nano-roughness were found to inhibit the settlement of Ulva spores and its antifouling effect was shown to exceed that of a commercially available fouling release coating (Majumdar et al., 2008). Superhydrophobic coatings with nano-scaled roughness prevented the settlement of major micro- and macro-fouling species (Scardino et al., 2009). On another hand, engineered nanomaterials have found extensive application in electronics, pharmaceuticals, renewable energies, and antifouling coatings applications, amongst others (Bandala and Berli, 2019). Hybrid nanocomposites of organic–inorganic materials give an opportunity to combine the characteristics of different materials generating opportunities to prevent biofouling (Wassel et al., 2020; Nathanael and Kumar, 2021). Metal and metal oxide nanoparticles, such as silver (Ag), titanium dioxide (TiO$_2$) and zinc oxide (ZnO), possess antifouling properties (Kim et al., 2003; Chapman et al., 2016; Das et al., 2013; Song et al., 2020). Additionally, carbon nanotubes (CNTs) incorporated in coatings prevent macrofouling by inhibition of settlement and adhesion of larvae (Carl et al., 2012; Kim et al., 2014; Yang et al., 2016a; Kim et al., 2016; Aghajani and Esmaeili, 2021).

Nanostructured metal oxide, like ZnO and TiO$_2$, is capable of absorbing visible and ultraviolet light and inhibiting microbial growth due to the photocatalytic process leading to redox reactions (Baruah et al., 2012; Danwittayakul et al., 2018; Spirescu et al., 2021). The generated reactive oxygen species (ROS) like peroxides, superoxides, and hydroxyl radicals that form during photocatalysis, prevent the growth of microorganisms on the surfaces (Sathe et al., 2017; Ganguly et al., 2018). Metal oxide nanostructures can have advantages in antifouling application than other types of nanocoatings due to the fact that ROS are short-lived and have localized surface toxicity (Bora et al., 2017). Antifouling and anti-algal activities of coatings containing ZnO nanorods and TiO$_2$ nanoparticles have been recently studied (Al-Fori et al., 2014; Sathe et al., 2016b; Yemmireddy and Hung, 2017; Zhu et al., 2018).

This review is aimed at providing an overview of recent advances in formulation and antifouling activity of nanocoatings containing active ingredients of polymers, inorganic nanoparticles, or organic-inorganic hybrid materials.

**NANOTECHNOLOGY-BASED ANTIFOULING SOLUTIONS**

Various antifouling strategies, namely fouling-resistant, fouling-release and fouling-degrading, have been explored in preparation of antifouling coatings (Figure 1) to cater for treatment of different types of biofoulings. For instance, fouling-resistant coatings with a highly hydrated surface provide a physical and free-energy barrier to prevent adhesion of foulants such as proteins, algae, or bacteria (Thérien-Aubin et al., 2011). In contrast, the fouling-release coatings allow weak adhesion of foulant, which can be removed afterwards by external force like water flushing (Damodaran and Murthy, 2016). These two coating approaches introduce hydrophilic and hydrogen bond-forming characteristics to the surface, where the tightly bound water molecules form a barrier layer preventing adsorption (Chen et al., 2010). The third type, fouling-degrading coatings, incorporates antimicrobial moieties in the coating to degrades the settled bacteria or microorganisms via oxidation or other bactericidal functionalities (Sakala and Reches, 2018).

**Antifouling Biocides**

Antifouling biocides are chemicals that can destroy or render harmless the microorganisms responsible for biofouling. The previously widely used tri-substituted organostannic compounds, such as tributyltin (TBT) and triphenyltin (TPT), in antifouling paints on ships are no longer permitted for use as biocides within the EU since July 2010 (EU Commission Regulation, 2010), due to the risk of leaching into the aquatic environment and toxicity to aquatic organisms through endocrine disruptive effects. On the other hand, copper compounds are used in antifouling paints for centuries to control hard fouling, such as barnacles, mussels and tube worms, attributed to their effective, available and relatively inexpensive characters compared to other biocides. The most applied copper compounds are cuprous oxide, copper thiocyanate and copper flake, which are used in many different formulizations of antifouling paint. Similarly, copper leachate from antifouling paints has been found to impact water quality. Consequently, California’s department of pesticide regulation in the US has established a maximum allowable copper leach rate of 9.5 μg/cm$^2$/day for copper-based antifouling products intended for use on recreational vessels, which became effective on July 1, 2018 (California Notice, 2018).
And the state of Washington (US) has regulated to cease the use of copper-based paint for recreational boats by 2021 due to its toxicity to juvenile salmon. European Commission urges the member states to find and invest in alternatives. Apart from copper, organic booster biocides, such as chlorothalonil, dichlofluanid, chlorine dioxide DCOIT, Diuron, Irgarol 1051, TCMS pyridine, zinc pyrithione and Zineb (Guardiola et al., 2012; Venkatnarayanan et al., 2017), are introduced as alternatives to the restricted organotin compounds in antifouling products. However, some of the booster biocides appear to be persistent and have a continuous leaching character from antifouling paints, potentially posing a significant threat to the aquatic environment with risks of accumulation in aquatic products and development of antibiotic resistance in bacteria. Therefore, eco-friendly and non-biocide-release coatings for marine biofouling prevention are urgently needed.

**Polymer-Based Antifouling Coatings**

Surface PEGylation, i.e., grafting polyethylene glycol (PEG) to surfaces to develop linear PEG brushes, has long been a standard way to resist the adsorption of proteins (Li et al., 2019). The efficient repulsion of PEG brushes to foulants roots from the extensive hydration layer, the rapid conformational changes and steric repulsion (Hui et al., 2017). However, PEG has been found with short-term stability in biochemical environments due to readily subjected to oxidative degradation and enzymatic cleavage, that results in the formation of aldehyde-terminated chains and a subsequent reaction with amino-contained proteins (Chen et al., 2010). Moreover, PEG coatings used to swell in aqueous environments because of their highly hydrated nature, which deteriorates their mechanical strength, as well the chemically different substrates remain difficult for PEG to graft (Xie et al., 2019). Hence, studies on alternatives for PEG, such as polyoxazolines (Divandari et al., 2017), polyglycerol dendrons (Wyszogrodzka and Haag, 2009), polysaccharides (Rendueles et al., 2013), polypeptoids (Lin et al., 2011), polyacrylamide (Liu et al., 2012) and zwitterionic polymers (Knowles et al., 2017), has been conducted and these alternatives show similar or better fouling resistance. Besides linear polymer brushes, cyclic- and loop-structured polymer brushes based on poly(2-alkyl-2-oxazoline)s, such as poly(2-methyl-2-oxazoline) (POMXA) and poly(2-ethyl-2-oxazoline) (PEOXA), have been studied extensively they can generate denser brushes and thus show better protein-resistant properties (Wang et al., 2019). However, it is still costly and complex to obtain the highly dense cyclic polymers brushes in large quantities for large-scale application.

Poly(dimethylsiloxane) (PDMS) coatings represent another type of antifouling mechanism with fouling-release character, attributed to the chemical inertness and low surface energy of PDMS elastomer (Dafforn et al., 2011). In addition, additive of non-reactive silicone oils provides lubricity to the coating surface and therefore considerably reduces fouling by deceiving the mechanosensing ability of fouling organisms, especially for mussels, deterring secretion of adhesive threads, and decreasing the molecular work of adhesion (Amini et al., 2017). To further increase the hydrophobicity of coating surface, a layer of polystyrene (PS) microspheres could be assembled on top of PDMS coating (see Figure 2) (Mo et al., 2021). As shown in Figure 2 (left part), fouling organisms can adhere to the surface of conventional silicone sample without PS microspheres, where it has more attachment points, and the fouling organisms usually show greater bonding strength. In contrast, on the surface of PS-sphere-coated PDMS (diffused with phenylmethylsilicone oil-PSO, right part in Figure 2), there are fewer attachment points and weakened bonding strength between fouling organism and coatings. Therefore, benthic diatoms are easily removed under the shearing force of seawater, so as to achieve the purpose of antifouling.

**Hydrogel Coatings for Antifouling**

Hydrogel is a polymer network which holds a high content of water (typically 80–90%). As aforementioned, many hydrophilic polymers like PEG and zwitterionic polymers can prevent attachment of various proteins, polysaccharides, and many microorganisms. However, hydrophilic polymers typically have difficulty in making surface coating due to the low adhesion strength to various substrates. Out of the approaches developed to
overcome this problem, hydrogel coatings are of especial interest because of their outstanding characters on both antifouling abilities due to superhydrophilicity and fouling-release properties due to the relatively low Young’s modulus to destabilize the attachment of marine organisms (Brady and Singer, 2000). To render their practical application in marine antifouling, improvement of the adhesion strength of hydrogels has been investigated through surface covalent cross-linking (Gao et al., 2020) or by decoupling polymerization from crosslinking and interlinking, hydrogel paints were prepared and applied on various substrates by various operations (brush, cast, dip, spin, or spray) (Yao et al., 2019; Yang et al., 2021). The advantages of hydrogel paint lie in the ease of application, like a common paint, without involving mold, UV light, or oxygen-free environment. Secondly, the hydrogels are commonly made by free-radical polymerization and are readily copolymerized with silanes or hydroxyl-contained molecules. While, the substrate materials, such as glasses, metals, ceramics, or organic elastomers and plastics, have hydroxyl groups on their clean surfaces or can be easily acquired through surface plasma treatment, which results in high adhesion strength. Thirdly, dried hydrogel paint can be ground into powders and redissolved in water for application, and the extended shelf life greatly amplifies the advantage of hydrogel paint.

Inorganic Ingredient-Based Coatings for Prevention of Biofouling

Antifouling marine paints containing nanomaterials have been reported to offer super hydrophobicity, high durability, water repellent, anti-sticking, microbial resistance, elastomeric, and anti-corrosive properties (Yebra et al., 2006; Callow and Callow, 2011), which are novel solutions for the sustainable growth of maritime industries. Nanoparticles can be used efficiently in formulations of antifouling coatings resulting in improved properties (Lakhotia et al., 2018). Silver nanoparticles (AgNPs) (Kumar et al., 2017; Kumari et al., 2017), carbon nanostructures like carbon nanotube (CNT) (Dasgupta et al., 2017) and graphene (Bystrov et al., 2017) are commonly used for antifouling prevention. Additionally, several metal oxides semiconductors like titanium dioxide (TiO₂) (Kim et al., 2016), and zinc oxide (ZnO) (Al-Naamani et al., 2017; Kumar et al., 2019a) nanoparticles have been used for nanocomposite formulations showing antifouling activities. The analysis of literature suggests that most of antifouling studies were dealing with metal oxide nanostructures, such as ZnO and TiO₂ (Figure 3). Less attention is given to carbon nanostructures such as CNT. Below we reviewed the antifouling activity of nanosilver, carbon nanostructures and nanostructured metal oxides as well as composite nanocoatings.

Silver Nanoparticles

Silver-based coatings or silver deposited surfaces are well-known to provide bacteriostatic/bactericidal, fungistic/fungicidal and
Silver is known to have inhibitory effects against different kinds of microorganisms (Goswami et al., 2015; Kumari et al., 2016; Naskar et al., 2018). Therefore, it finds applications in medical and consumer products, and in environmental applications (Kumar et al., 2014; Rasheed et al., 2017). Nano-sized silver, i.e., silver nanoparticles, have found increasing application as an antimicrobial agent due to high surface to volume ratio and increased surface reactivity (Kumari et al., 2016). Several studies about the antimicrobial activity of silver nanoparticles and their action mechanism have been reported (Kumar et al., 2014; Durán et al., 2016). Silver formulations containing silver ions or silver nanoparticles are generally considered biologically benign and safer than any other heavy metal-based formulations (Rasheed et al., 2017). The bacteriostatic/bactericidal properties of nanosilver can also be useful in antifouling applications against microfouling (Devasconcellos et al., 2012; Li et al., 2013). Only a few studies investigated the effect of nanosilver on eukaryotes or macrofouling organisms. For example, it has been shown that a silver nanoparticle coating prevents the adhesion of marine and freshwater algae (Ren et al., 2014). In another study, nanosilver prevented mussel settlement through modification of the structure of biofilms (Yang et al., 2016b).

The mechanism of the antifouling properties of silver nanoparticles is not yet clear and debatable. One of the most accepted mechanisms is based on the ability of Ag⁺ ions to anchor to cell walls. It is shown that Ag⁺ ions penetrate into the bacterial cell and interacts with thiol groups of most of the vital enzymes, leading to deactivation of the enzyme, which ultimately stops bacterial growth leading to the death of the bacterial cell (Kim et al., 2007; Kumar et al., 2014; Pareek et al., 2018). The study with eukaryotes suggested that contact killing of the cells by Ag⁺ ions is the main antifouling mechanism (Ren et al., 2014). The formation of free radicals by AgNPs is another proposed mechanism. Electron spin resonance (ESR) spectroscopy studies suggested that free radicals generated from AgNPs damage cell membranes when they come in contact with bacteria, resulting in membrane rupture and ultimately cell death (Danilczuk et al., 2006; Kailasa et al., 2019). However, antimicrobial activity of AgNPs depends on several factors including physico-chemical parameters such as size (Ginjupalli et al., 2018; Kumar et al., 2019b), morphology (El-Zahry et al., 2015), crystallinity (Kumar and Münstedt, 2005), surface coatings of nanoparticles (Brobbey et al., 2019), and microbial species in the environment (Pareek et al., 2018).

**Graphene and Carbon Nanotube**

Graphene is an allotrope of a single layer of carbon atoms arranged in a sp²-bonded hexagonal lattice (Figure 4). They are naturally found as the building blocks of graphite. Graphene materials show high specific surface area, electron conductivity and thermal stability that make it attractive for several environmental applications like photocatalysis, energy production and storage (Sun et al., 2015; Ozer et al., 2017; Xu et al., 2018). Carbon nanotubes (CNTs) represent a hollow, concentric cylindrical structure, typically with a diameter of a few nanometers and a length varying from a few nanometers to several microns (100 μm) up to a few millimeters (4 mm) (Venkataraman et al., 2019). Nanotubes are primarily classified into three categories; single-walled carbon nanotubes (SWCNTs), double-wall carbon nanotubes (DWCNTs), and multi-walled carbon nanotubes (MWCNTs). The environmental application of CNT’s mainly involves the fabrication of nanocomposite materials with biocidal properties and fouling release activities (Upadhyayula and Gadhamshetty, 2010; Dasgupta et al., 2017).

**Carbon Nanotube**

**Graphene**

CNTs and graphene exhibit good antimicrobial activity towards both Gram-positive and Gram-negative bacteria as well as bacterial spores (Łukowiak et al., 2016; Al-Jumaili et al., 2017; Sun et al., 2020). CNTs, especially SWCNTs were shown to have significantly greater antibacterial activity than MWNTs, probably due to their smaller sizes, enabling membrane perturbation (Figure 5) (Kang et al., 2008). Additionally, CNTs can impact the recruitment of macro-fouling organisms (Beigbeder et al., 2008). Nano-sized carbon black more effectively prevented settlement of the barnacle *Amphibalanus amphitrite* larvae compare to single-layer graphene oxide (Mesarić et al., 2013). Just 0.5% weight percent of CNT affected the composition of biofilms by increasing the abundance of Proteobacteria and decreasing the abundance of Bacteroidetes, which in turn decreased the settlement of *Mytilus coruscus* (Yang et al., 2016a).
One of the first CNT-based antifouling coatings was developed in 2008 (Beigbeder et al., 2008). It was based on the incorporation of synthetic multi-wall CNTs in silicone coatings. Nowadays, CNT-based coatings are actively used as antifouling and anti-corrosion marine coatings in the construction and oil and gas industries (Dustebek et al., 2016). CNTs are generally loaded into corrosion marine coatings in the construction and oil and gas industries (Dustebek et al., 2016). CNTs are generally loaded into corrosion marine coatings in the construction and oil and gas industries (Dustebek et al., 2016). CNTs act as an efficient adsorbent due to their large surface area, π-bond electrons on the surface, providing more chemically active sites on the nanotubes, and hollow and layered structures. CNTs have high tensile strength and Young’s modulus, and in comparison to steel, CNTs have hundreds and tens of times the higher tensile strength and Young’s modulus (Walters et al., 1999). The reinforcement of the paint matrix with CNTs improves mechanical properties in the coatings/paints. Dustebek et al. (Dustebek et al., 2016) investigated the effect of CNTs on the mechanical strength of a self-polishing antifouling resin-based paint and found that the increase in the amount of MWCNT leads to an improvement in the mechanical strength of self-polishing antifouling paints. Antifouling paints with 0.5% (w/w) and 0.7% (w/w) of MWCNTs showed a significant improvement in impact resistance (Dustebek et al., 2016). This study was further supported by another research that evaluated the effect of reinforcement of MWCNT and graphene oxide (GO) on mechanical properties of poly-dimethyl siloxane (PDMS) marine coatings (Cavas et al., 2017). Incorporation of MWCNTs in composites increased both tensile strength and percent of elongation of PDMS marine coatings. These studies indicate that CNT and GO beside of antifouling properties can improve the mechanical properties of nanocomposite coatings.

Numerous mechanisms of antifouling action of CNTs and GO have been proposed, but the actual mechanism is still not clear. A study suggested that different antifouling mechanisms can be involved (Mesarič et al., 2013). First, CNTs and GO are toxic to microbes and larvae of macrofouling organisms. The toxic effect of CNTs is widely known (Francis and Devasena, 2018). CNTs can increase cell apoptosis, oxidative stress, and inflammation. Second, CNTs and GO can inhibit larval settlement by a non-toxic way simply interfering with the attachment and adhesion of cyprid larvae (Mesarič et al., 2013).

The physical size (in particular the length), diameter, surface area, concentration, treatment time, etc., play a role in the antifouling activity of CNTs. Yang et al. (2010) investigated the effect of length of SWCNTs’ on antimicrobial activity to Salmonella cells using three different lengths of SWCNTs (<1 μm, 1–5 μm, and ca.5 μm) (Yang et al., 2010). Longer SWCNTs were reported to exhibit stronger antimicrobial activity by aggregating bacterial cells more effectively, whereas shorter SWCNTs were reported to aggregate between themselves without involving many bacterial cells (Figure 6). The tube diameter also plays an important task in the inactivation of microorganisms. Smaller diameters CNTs (<10 nm) can damage cell membranes by interaction with the cell-surface, while large diameter CNTs (15–30 nm) mostly interact by their sidewalls with the bacteria (Upadhyayula and Gadhamshetty, 2010).

### Metal Oxides and Metal/Metal Oxide Hybrid Nanostructure

Metal oxide nanoparticles (NPs), such as ZnO, TiO₂, SnO₂, are highly photoactive and used for antimicrobial, self-cleaning, self-healing, anti-corrosion and anti-biofouling applications. Table 1 summarizes the antifouling effects of various photocatalytic metal oxide nanostructures on aquatic prokaryotes (bacteria) and eukaryotes (microalgae, barnacles, bryozoans, etc.). In general, investigators studied the antifouling effect of metal oxide nanoparticles, nanowires, nanorods, and hybrid nanostructures. ZnO, TiO₂ and hybrid metal-metal oxide, as well as hybrid carbon-metal oxides nanostructures were the most commonly used systems for the inhibition of biofouling (Table 1). ZnO nanoparticles have attracted more attention compared to other metal oxides due to their low cost and ready availability (Naskar et al., 2018; Wallenhorst et al., 2018). As per the FDA (Food and Drug Administration, United States) guidelines, ZnO is listed as a safe material for various uses. ZnO NPs are used in the food processing and packaging, as well as in the agriculture sector because of their biocompatibility, low toxicity and antimicrobial properties (Garcia et al., 2018). Photocatalysis of various toxic organic dyes and inorganic pollutants in industrial wastewater has been performed using ZnO and TiO₂ semiconductor oxides under light irradiation. TiO₂ is widely used in self-cleaning...
coatings and paints but their application is limited to outdoors, as they require activation by UV light (Xu et al., 2017; Adachi et al., 2018). The most common bacteria used for testing include Gram-positive (B. subtilis, Micrococcus) and Gram-negative (E. coli, P. aeruginosa) pathogens (Table 1). In opposite, the most common eukaryotes used in metal oxide nanostructures studies are environmental species of microalgae and invertebrate larvae.

Silver nanoparticles is a mostly used antimicrobial agent that synthesized with environment-friendly methods and can be non-toxic for mammals. Titanium oxide nanotubes have been used to improve the functional properties of silver nanoparticles because of their superior specific surface area both on inner and outer surfaces of the tubular structure. Yee et al., 2017 proposed an innovative 2-steps hydrothermal synthesis of a silver–titania nanotube (Ag/TNT) composite that showed nanotubular TiO₂ structures with Ag nanoparticles uniformly dispersed throughout the nanomaterial (Yee et al., 2017). The inhibitory properties of the composite material against biofilm were studied and the result demonstrated the Ag/TNT reduced the biofilm formation of marine bacterium Halomonas pacifica by 98% compared to bare titania nanotubes. Additionally, Ag/TNT also showed growth inhibition of marine microalgae Dunaliella tertiolecta and Isochrysis sp (Yee et al., 2017). A ternary nanocomposite (PDMS/GO-Al₂O₃ NRs) superhydrophobic coatings were also developed from PDMS, and graphite oxide anchored with alumina nanorods (GO-Al₂O₃ NRs) hybrid sheet via solution-casting method (Selim et al., 2018; He et al., 2021). The results showed that the well-dispersed GO-γ-AlOOH NRs hybrid sheets increased the contact angle (151°), decreased the surface free energy (13.25), and improve micro-nano roughness on the surface, and thus the developed nanocomposites may have promising antifouling applications in the shipping industry (Selim et al., 2018). In a recent study, silicone/graphene-based two novel superhydrophobic nanocomposite were developed, and the results shows PDMS/GO-γ-AlOOH nanorod composite had better antibacterial activity than PDMS/RGO nanocomposite against different bacterial strains might be due high surface area and stabilizing effects of the GO-γ-AlOOH hybrid nanofillers. The GO-γ-AlOOH (3 wt%) nanostructured coating had profound superhydrophobic antifouling properties due to their homogeneity, and high WCA of 151° and a rough surface (Selim et al., 2022).

Aluminum oxides are inexpensive, non-toxic, and one of the most stable inorganic materials. Boehmite is an aluminum oxide hydroxide (γ-AlOOH) particle that contain hydroxyl groups on its surface. Boehmite nanoparticle has the orthorhombic structure, in which the boehmite nanoparticles’ surface are covered with OH groups. Boehmite nanoparticles can improve hydrophilicity and surface properties of the membrane due to presence of extra hydroxyl groups on their surface, and thus reduce fouling of the resulted membranes (Vatanpour et al., 2012; Farjami et al., 2021). Among the alumina compounds, boehmite has highest hydrated surface and hydrophilicity. The effects of two different solvents, dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP) were evaluated on performance of the pristine and EPVC/nano-boehmite nanocomposite membranes, and the results showed that the membranes prepared in NMP solvent using boehmite

![FIGURE 6](https://www.frontiersin.org/articles/10.3389/fnano.2021.771098/full/#fig6) | SEM images of Salmonella (A) without SWCNTs, and treated with SWCNTs of (B) < 1 μm (C) 1–5 μm, and (D) > 5 μm. Reproduced with permission from (Yang et al., 2010).
Antifouling properties and toxicity of metal oxide nanostructures. Nanocoating for Biofouling Prevention

**TABLE 1** | Antifouling properties of common metal oxide nanostructures.

| Nanostructure        | Organisms                                          | Mechanisms                                         | Applications                              | References                      |
|----------------------|----------------------------------------------------|----------------------------------------------------|-------------------------------------------|----------------------------------|
| **Prokaryotes**      |                                                    |                                                    |                                           |                                 |
| TiO$_2$ nanoparticles | *Stenotrophomonas maltophilia*                     | Photocatalytic effects                             | Marine underwater archaeological sites    | Ruffolo et al. (2013)            |
| TiO$_2$ nanofibers   | *Micrococcus sp.*                                   | Photo-degradation and inhibition of microbial      | Antifouling effects under visible light   | Ademola                         |
|                      |                                                    | growth properties of polyacrylonitrile - TiO$_2$  |                                           | Bode-Aluko et al. (2021)         |
| Ag-TiO$_2$ hybrid     | *Halomonas pacifica*                                | Reduced biofilm attachment by 98%                 | Antimicrofouling effect                   | Yee et al. (2017)               |
| Ag@TA-SiO$_2$         | *Escherichia coli*                                  | Coating suppressed 98.6% of protein adsorption,   | Antimicrofouling effect                   | Deng et al. (2021)              |
| nanoparticles         |                                                    | and antibacterial efficiency by 98.1 and 82.7%    |                                           |                                 |
| ZnO nanoparticles     | *S. aureus*                                         | Photocatalytic and toxic effects                   | Prevention of microfouling on glass       | Valenzuela et al. (2019)         |
|                      | *S. aureus (bacterium)*                            |                                                    | surfaces                                 | Bojarska et al. (2017)          |
| ZnO nanowires         | *Bacillus subtilis*                                 | Cell membrane modification, and ROS production    | Photocatalysis, Antimicrobial agents      |                                 |
| ZnO nanorods          | *Escherichia coli*                                  | ROS production leads to oxidation of membrane     | Anti-biofouling activity                 | Al-Hinai et al. (2017)          |
|                      |                                                    | lipids causing damage of membrane and cell lysis  |                                           |                                 |
| ZnO nanostructures    | *Pseudomonas aeruginosa*                            | Generation of ROS increases with increased        | Enhanced biofouling resistance           | Rasmie et al. (2018)            |
|                      |                                                    | oxygen vacancies resulting in enhanced            |                                           |                                 |
| MgO nanoparticles     | *Escherichia coli* Saltmonella enterica             | Damage cell membrane leading to intracellular     | Antifouling food surfaces                | Jin and He, (2011)              |
|                      |                                                    | contents leakage                                   |                                           |                                 |
| Al$_2$O$_3$ nanoparticles | *Escherichia coli*                                 | Cell wall disruption because of tiny particle     | Antifouling coating having              | Dong et al. (2015)              |
|                      |                                                    | size and high surface energy                       | anti-adhesion ability                    |                                 |
| PDMS/GO-Al$_2$O$_3$ NR | *Pseudomonas aeruginosa*                            | Formation of micro-nano roughness, lower surface  | Superhydrophobic self-                  | Selim et al. (2018)             |
|                      | *Micrococcus sp., Pseudomonas putida,*             | free energy                                        | cleaning antifouling surface             |                                 |
| CeO$_2$ nanoparticles | *Pseudomonas aeruginosa*                            | Cell stress leading to cell death                  | Anti-infection applications              | Alpaslan et al. (2017)          |
|                      | *Staphylococcus epidermidis*                        |                                                    |                                           |                                 |
| Graphene oxide (GO)   | *Bacillus sp.*                                      | Significant reduction of biofilm and biomass      | Anti-biofouling and anti-               | Balakrishnan et al. (2021)      |
| nanoparticles         |                                                    | thickness                                          | corrosion properties                     |                                 |
|                      |                                                    |                                                    |                                           |                                 |
| **Eukaryotes**        |                                                    |                                                    |                                           |                                 |
| TiO$_2$ solution      | *Chlorella mirabilis*                               | Photocatalytic degradation in presence of UV light| Clay bricks                              | Graziani et al. (2014)          |
| TiO$_2$ nanoparticles | *Chroococcidiopsis fissaursarum* (microalgae)       | Ribelet surface structure and hydrophobic         | Anti-biofouling surface                  | Li et al. (2020)                |
|                      |                                                    | wettability                                        | Prevent membrane fouling                 | Sathe et al. (2016a)            |
| ZnO nanoparticles     | *Dunaliella salina* (microalgae)                    | Formation of ROS                                   | Prevent fouling on glass substrata       | Al-Fori et al. (2014)           |
|                      |                                                    |                                                    | Prevent fouling on glass substrata       | Kumar et al. (2021)             |
| ZnO nanorods          | *Bugula neritina* (bryozoa)*                       | Formation of ROS                                   |                                           |                                 |
| ZnO–SnO$_2$ core–shell nanoparticles | *Tetraselmis sp. (microalgae)*                   | Formation of ROS                                   |                                           |                                 |
|                      |                                                    |                                                    | Prevent fouling on glass substrata       |                                 |
| TiO$_2$, and Nb$_2$O$_5$ nanoparticles | *Navicula spp. (Diatoms)*                     | Formation of ROS                                   | Prevent fouling on glass substrata       | Dineshram et al. (2009)         |
| Ag–TiO$_2$ hybrid     | *Dunaliella tertiolecta*                            | Antifouling activity                               | On fouling microalgae                    | Yee et al. (2017)               |
| Ag@TA–SiO$_2$         | *Nitzschia closterium*                              | Coating reduced attachment of microalgae *N.       | Prevent fouling                         | Deng et al. (2021)              |
| nanoparticles         |                                                    | closterium and D. zhanjiangensis by 93.5 and       |                                           |                                 |
|                      |                                                    | 97.6%, respectively                                |                                           |                                 |

Nanocoatings had higher anti-fouling and fouling resistance properties (Farjami et al., 2021). Antifouling properties and toxicity of metal oxide nanomaterials depend on the biological species, with some species being more sensitive than others (Dobretsov et al., 2020). Additionally, physico-chemical properties of nanomaterials such as particle size, shape, surface charges, and surface groups affect their toxicity. The smaller size of nanomaterials can easily enter through cell membranes and other barriers of the living organisms. The amount of uptake of nanomaterials decreases with the increased particle size (Hoshyar et al., 2016). The basic principle of metal oxide
Photocatalytic disinfection involves a generation of reactive species, typically ROS, which can harm aquatic microorganisms at varying levels. In a study by Al-Fori et al. (2014), ROS were observed to prevent biofouling by micro- and macro-organisms. Exposure of metal oxides to visible light results in the generation of ROS, which are capable of oxidizing a compound adsorbed on their surface and degrading it to less harmful byproducts or degrade them (Alahverdiyev et al., 2011; Carré et al., 2014; Khan et al., 2015). Similarly, ROS and metal anions prevent fouling by micro- and macro-organisms (Al-Fori et al., 2014). Production of ROS at low dosage levels results in harsh oxidative stress that causes the damage of genetic material such as DNA and RNA, oxidation of lipid, alteration of protein, inhibition of enzymes, etc. (Figure 7), while prokaryotic and eukaryotic cell death occurs at higher concentrations of ROS (Pan et al., 2010; Alahverdiyev et al., 2011; Carré et al., 2014). The generated ROS are short-lived and only affect organisms that come in direct contact with them (Bora et al., 2017).

Metal oxide nanorods and nanowires based photocatalytic coatings have attracted recent attention owing to its ease of controlled fabrication processes (Wei et al., 2005; Inderan et al., 2015; Jin et al., 2015a; Jin et al., 2015b; Wang et al., 2018). ZnO nanorod-based photocatalytic coatings have been found effective against micro- and macro-fouling on a glass substrate and fishing net substrates in the laboratory (Al-Fori et al., 2014; Spirescu et al., 2021) and field experiments, respectively (Sathe et al., 2017) (Figure 8). ZnO nanorods have increased stability, reduced loss of nanoparticles compared to ZnO nanoparticles and can be fabricated into various types of support materials (Al-Fori et al., 2014). Additionally, ZnO nanorods have lower toxicity compared to ZnO nanoparticles, which was confirmed by experiments with bacteria, microalgae, larvae of invertebrates and adult mussels (Falfushynska et al., 2019; Dobretsov et al., 2020).

**Inorganic-Polymer Nanocomposite Coatings for Prevention of Marine Biofouling**

Apart from purely polymer and organic molecule mixed coatings, organic/inorganic hybrid composites prepared by blending nano-sized inorganic fillers in polymer matrix have been investigated on the fouling-release and fouling-degrading performance. And the nanomaterial-based antifouling coatings have been proved as one of the most promising coatings for biofouling prevention, amongst others (Tobaldi et al., 2017). While metal oxide nanostructures are capable of preventing macro-fouling, their effectiveness is low due to their solubility. Additionally, nanoparticles can be lost and cause harmful effects on the environment. In order to enhance stability, reduce environmental impact, and enhance the antifouling effect, metal oxide nanostructures are usually attached to support substrata or incorporated into a stable matrix of coating. For example, ZnO nanorods attached to glass substrata was effective against the marine bacterium *Acinetobacter* sp., the marine microalgae *Tetraselmis* sp. and the bryozoan *Bugula neritina* under the artificial sunlight (Al-Fori et al., 2014).

Various nanostructure-based nanocomposite antifouling coatings reported in the literature are summarized in Table 2. ZnO and TiO2 nanoparticles are most commonly used, while...
Cu$_2$O, CuO and Al$_2$O$_3$ are also incorporated into nanocomposite coatings (Table 2). PDMS has certain advantages as a coating. It has a hydrophobic surface and, thus, used for fouling release antifouling applications (Zhang and Chiao, 2015). Biopolymers, such as chitosan, have been used to develop environmentally friendly nanocomposite antifouling coatings (Carteau et al., 2014; Krishnan et al., 2015; Pounraj et al., 2018). Chitosan and ZnO or TiO$_2$ based nanocomposite coatings have been reported as effective against several marine microorganisms including biofilm-forming bacterium Vibrio fischeri (Baniamerian et al., 2018), Pseudoalteromonas nigripaciens, and diatoms Navicula sp. (Al-Naamani et al., 2017). While metal oxides have photocatalytic properties that prevent biofouling at the light, the addition of chitosan enhances antifouling properties in dark conditions. Most of the studies with ZnO nanoparticles or nanorods nanocomposite antifouling coatings were conducted in the laboratory conditions (Table 2). Since in the field there are many different species of biofouling organisms, as well as
coatings are exposed to different physical and biological factors, it is important to test coatings the field conditions in order to prove their antifouling activity.

**CONCLUDING REMARKS AND PERSPECTIVES**

Biofouling is a major problem for maritime industries constantly affecting marine installations. Traditional antifouling methods are mainly based on the applications of biocidal agents that detract or kill organisms close to vicinity, which is apparently not environment friendly. This review summarized polymeric and polymer-inorganic composite alternatives to toxic antifouling paints, that show marine antifouling effects via fouling resistant, release, or degrading mechanisms. For polymer and hydrogel antifouling coatings, surface chemistry and coating techniques often determine the antifouling performance. For inorganic-polymer nanocomposite, the intrinsic characteristics of inorganic nanoparticles is responsible for fouling degradation. In photocatalytic nanostructure-based antifouling applications, ROS generated by photocatalytic nanostructures in presence of light can kill /inactivate micro- and macro-organisms. Compared to toxic biocides, the generated ROS are short-lived and only affect organisms that are in close proximity of the coatings. Thus, photocatalytic nanocoatings are less toxic to aquatic organisms compared to traditional antifouling coatings. Metal oxide nanostructure-based coatings are being considered as one of the promising environment-friendly antifouling technologies strategies that is suitable for marine applications. In contrast, only a few studies that reported inhibition of macro-fouling in the field conditions have been conducted. This could be due to the deteriorated efficiency of nanocomposites antifouling coatings in the field or the difficulties in scaling up such coatings.
An ideal antifouling coating is expected to be durable, reliable, easily applicable, cost-effective, eco-friendly, and substrate-independent. It remains very challenging to realize all the desirable requirements simultaneously. No single chemistry/strategy has yet been identified as the universal antifouling method. Instead, one multifunctional coating with synergetic strengths by combining several antifouling strategies is probably the correct way reaching the goal of a successful antifouling coating. With the large amount of high-quality and sophisticated research that is being performed, zwitterionic polymers attract much attention in the development of next-generation antifouling materials, due to the simplicity of synthesis, ease of applicability, abundance of raw materials and availability of functional groups. At the same time, inorganic nanomaterials possess great advantage in preparation and application for antifouling. Therefore, the inorganic-polymer composite coatings represent another potentially commercial solution, especially considering their effectiveness and low cost. However, it is still necessary to develop new polymers or composite to improve the antifouling performance, especially focusing on long-term durability when used in both static and dynamic environments. Apart from the efficiency enhancement, coating techniques also need to be developed in order to successfully translate these coatings toward large-scale applications to find their way outside the lab. Hence, the frequently used chemical grafting approaches need to be simplified, in order to cope with the physiosorption techniques for coating, often by layer-by-layer or spray-painting. Combining simple coating techniques with a self-replenishing antifouling character to enhance antifouling durability and crosslinkers or catch-bonds to enhance mechanical stability, could result in technologically mature antifouling coatings with large-scale applicability in real maritime environmental conditions and on different materials such as vessels, fishing nets, and pipes. Finally, the impacts of environmental toxicity of such coatings should be more thoroughly investigated.

AUTHOR CONTRIBUTIONS

SK, and JD contributed to conception and design of the study. SD and FY organized the database. SK and FY wrote the first draft of the manuscript. All authors contributed to manuscript revision, read, and approved the submitted version.

ACKNOWLEDGMENTS

SK acknowledged Department of Biotechnology (DBT), Government of India for financial support (sanction letter vide no. BT/20/NE/2011) through “Biotechnology Overseas Associateship Award for NER Scientists”.

REFERENCES

Adachi, T., Latthe, S. S., Gosavi, S. W., Roy, N., Suzuki, N., Ikari, H., et al. (2018). Photocatalytic, Superhydrophilic, Self-Cleaning TiO2 Coating on Cheap, Light-Weight, Flexible Polycarbonate Substrates. Appl. Surf. Sci. 458, 917–923. doi:10.1016/j.apsusc.2018.07.172

Ademola Bode-Aluko, C., Pereao, O., Kyaw, H. H., Al-Naamani, L., Al-Abri, M. Z., Tay Zar Myint, M., et al. (2021). Photocatalytic and Antifouling Properties of Electrosprun TiO2 Polyacrylonitrile Composite Nanofibers under Visible Light. Mater. Sci. Eng. B 264, 114913. doi:10.1016/j.mseb.2020.114913

Aghajani, M., and Esmaeili, F. (2021). Anti-biofouling Assembly Strategies for Protein & Cell Repellent Surfaces: a Mini-Review. J. Biomater. Sci. Polym. Educ. 32, 1770–1789. doi:10.1080/09205063.2021.1932357

Al-Fori, M., Dobretsov, S., Myint, M. T. Z., and Dutta, J. (2014). Antifouling Properties of Zinc Oxide Nanorod Coatings. Biofouling 30, 871–882. doi:10.1080/08927014.2014.942297

Ali, M. H., Sathe, P., Al-Abri, M. Z., Dobretsov, S., Al-Hinai, A. T., and Dutta, J. (2017). Antimicrobial Activity Enhancement of Poly(ether Sulfone) Membranes by In Situ Growth of ZnO Nanorods. ACS Omega 2, 3157–3167. doi:10.1021/acsomega.7b00314

Al-Jumaili, A., Alancherry, S., Bazaka, K., and Jacob, M. (2017). Review on the Antimicrobial Properties of Carbon Nanocomposites. Materials 10, 1066. doi:10.3390/ma10091066

Al-Naamani, L., Dobretsov, S., Dutta, J., and Burgess, J. G. (2017). Chitosan-zinc Oxide Nanocomposite Coatings for the Prevention of marine Biofouling. Chemosphere 168, 408–417. doi:10.1016/j.chemosphere.2016.10.033

Allahverdiyev, A. M., Abamar, E. S., Bagirova, M., and Rafailovich, M. (2011). Antimicrobial Effects of TiO2 and Ag2O Nanoparticles against Drug-Resistant Bacteria and Leishmania Parasites. Future Microb. 6, 933–940. doi:10.2217/fmb.11.78
Characterization and Reactivity. *Appl. Surf. Sci.* 391, 457–467. doi:10.1016/j.apsusc.2016.04.130

Boo, T., Sathe, P., Laxman, K., Dobretsov, S., and Dutta, J. (2017). Defect Engineered Visible Light Active ZnO Nanorods for Photocatalytic Treatment of Water. *Catal. Today* 284, 11–18. doi:10.1016/j.cattod.2016.09.014

Brady, R. F., and Singer, I. L. (2000). Mechanical Factors Favoring Release from Fouling Release Coatings. *Biofouling* 15, 73–81. doi:10.1080/09270109.2017.1295745

Brobey, K. J., Haapanen, J., Mäkelä, J. M., Gunell, M., Eerola, E., Rosqvist, E., et al. (2019). Effect of Plasma Coating on Antibacterial Activity of Silver Nanoparticles. *Thin Solid Films* 672, 75–82. doi:10.1016/j.tsf.2018.12.049

Bystrov, V. S., Bdklin, I. K., Siblin, M. V., Karpinsky, D. V., Kopyl, S. A., Goncalves, G., et al. (2017). Graphene/graphene Oxide and Polyyinlylidene Fluoride Polymer Ferroelectric Composites for Multifunctional Applications. *Ferroelectrics* 509, 124–142. doi:10.1080/00150193.2017.1295745

California Notice (2018). 2018-03, Final Decision Concerning Reevaluation of Copper Based Antifouling Paint Pesticides. CA, US: Department of Pesticide Regulation.

Callow, J. A., and Callow, M. E. (2011). Trends in the Development of Environmentally Friendly Fouling-Resistant Marine Coatings. *Nat. Commun.* 2, 244. doi:10.1038/ncomms1251

Carl, C., Poole, A. J., Vucko, M. J., Williams, M. R., Whalan, S., and De Nys, R. (2014). TiO2 Photocatalysis Damages Lipids and Proteins in *Mytilus galloprovincialis* using Nano Lighters Fluids and Organostannic Compounds. *Toxicol. Ind. Health* 30, 258–266. doi:10.1080/00150193.2017.1295745

Charnley, J., Weir, E., and Regan, F. (2010). Period Four Metal Nanoparticles on Surface of Silicone Elastomer. *Carbon Fiber Composite.*

Chapman, J., and Callow, M. E. (2011). Trends in the Development of Environmentally Friendly Fouling-Resistant Marine Coatings. *Nat. Commun.* 2, 244. doi:10.1038/ncomms1251

Chen, S., Li, L., Zhao, C., and Zheng, J. (2010). Surface Hydration: Principles and Characterization and Reactivity. *Appl. Surf. Sci.* 391, 457–467. doi:10.1016/j.apsusc.2016.04.130

Chung, S. H., and Manthiram, A. (2019). Current Status and Future Prospects of Polymer Brushes. *Macromolecules* 50, 7760–7769. doi:10.1021/acs.macromol.7b01720

Deng, Y., Song, G.-L., Zheng, D., and Zhang, Y. (2021). Fabrication and Synergistic Antibacterial and Antifouling Effect of an Organic/inorganic Hybrid Coating Embedded with Nanocomposite Agi2TA-SiO Particles. *Colloids Surf. A: Physicochemical Eng. Aspects* 613, 126085. doi:10.1016/j.colsurfa.2020.126085

Deshamant, R., Subasri, R., Somaraju, K. R. C., Jayaraj, K., Vedaprakash, L., Ratnam, K., et al. (2009). Biofouling Studies on Nanoparticle-Based Metal Oxide Coatings on Glass Coupons Exposed to marine Environment. *Colloids Surf. B: Biointerfaces* 74, 75–83. doi:10.1016/j.colsurfb.2009.06.028

Divandari, M., Morgese, G., Trachsel, L., Romio, M., Dehghani, E. S., Rosenboom, J.-G., et al. (2017). Toxicity Effects of Different Zinc Oxide Nanomaterials at 3 Trophic Levels: Implications for Development of Low-Toxicity Antifouling Agents. *Environ. Toxicol. Chem.* 36, 1343–1354. doi:10.1002/etc.4720

Dong, L.-X., Yang, H.-W., Liu, S.-T., Wang, X.-M., and Xie, Y. F. (2015). Fabrication and Anti-biofouling Properties of Alumina and Zeolite Nanoparticle Embedded Ultrafiltration Membranes. *Desalination* 365, 70–78. doi:10.1016/j.desal.2015.02.023

Durán, N., Durán, M., De Jesus, M. B., Seabre, A. B., Fávaro, W. J., and Nakazato, G. (2016). Silver Nanoparticles: A New View on Mechanistic Aspects on Antimicrobial Activity. *Nanomed.: Nanotechnol. Biol. Med.* 12, 789–799. doi:10.1016/j.nano.2015.11.016

Dustebek, J., Kandemir-Cavas, C., Nitodas, S. F., and Cavas, L. (2016). Effects of Carbon Nanotubes on the Mechanical Strength of Self-Polishing Antifouling Paints. *Prog. Org. Coat.* 96, 18–27. doi:10.1016/j.porgcoat.2016.04.020

El-Zahry, M. R., Mahmoud, A., Refaat, I. H., Mohamed, A. H., Bohlmann, H., and Lendl, B. (2015). Antibacterial Effect of Various Shapes of Silver Nanoparticles Monitored by SERS. *Talanta* 138, 183–189. doi:10.1016/j.talanta.2015.02.022

EU Commission Regulation (2010). EU COMMISSION REGULATION No 276/2010 of 31 March 2010, Amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as Regards Annex XVII (Dichloromethane, Lamp Oils and Grill Lighter Fluids and Organostannic Compounds).

Falkus, R., Wu, F., Ye, F., Kaisinruck, N., Dutt, J., Dobretsov, S., et al. (2019). The Effects of ZnO Nanostuctures of Different Morphology on Toxicity of Different Zinc Oxide Nanomaterials at 3 Trophic Levels: Implications for Development of Low-Toxicity Antifouling Agents. *Environ. Toxicol. Chem.* 36, 1343–1354. doi:10.1002/etc.4720

Farjami, M., Moghadassi, A., and Vatanpour, V. (2021). In *Nanofiltration Membranes.*

Faulkner, T. A., Casas, D. V., Kasianchuk, N., Dutta, J., Dobretsov, S., et al. (2019). The Effects of ZnO Nanostuctures of Different Morphology on Toxicity of Different Zinc Oxide Nanomaterials at 3 Trophic Levels: Implications for Development of Low-Toxicity Antifouling Agents. *Environ. Toxicol. Chem.* 36, 1343–1354. doi:10.1002/etc.4720

Fei, Z., Rodin, A. S., Andreev, G. O., Bao, W., McLeod, A. S., Wagner, M., et al. (2012). Gate-tuning of Graphene Plasmons Revealed by Infrared Nano-Imaging. *Nature* 487, 84–85. doi:10.1038/nature11253

Francis, A. P., and Devasena, T. (2018). Toxicity of Carbon Nanotubes: A Review. *Toxicol. Ind. Health* 34, 200–210. doi:10.1080/0748237717747472

Ganguly, P., Byrne, C., Breen, A., and Pillai, S. C. (2018). Antibimocial Activity of Photocatalysts: Fundamentals, Mechanisms, Kinetics and Recent Advances. *Appl. Catal. B: Environ.* 225, 51–75. doi:10.1016/j.apcatb.2017.11.018

Gao, L., Ma, S., Ma, Z., Zheng, Z., Zhou, F., and Liang, Y. (2020). In Situ covolent Bonding in Polymerization to Construct Robust Hydrogel Lubrication Coating on Surface of Silicone Elastomer. *Colloids Surf. A: Physicochemical Eng. Aspects* 599, 124753. doi:10.1016/j.colsurfa.2020.124753

García, C. V., Shin, G. H., and Kim, J. T. (2018). Metal Oxide-Based Nanocomposites in Food Packaging: Applications, Migration, and Regulations. *Trends Food Sci. Technol.* 82, 21–31. doi:10.1016/j.tifs.2018.09.021

Kumar et al. Nanocoating for Biofouling Prevention
