Hybrid Sol–gel Coatings for Corrosion Mitigation: A Critical Review

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Abstract: The corrosion process is a major source of metallic material degradation, particularly in aggressive environments, such as marine ones. Corrosion progression affects the service life of a given metallic structure, which may end in structural failure, leakage, product loss and environmental pollution linked to large financial costs. According to NACE, the annual cost of corrosion worldwide was estimated, in 2016, to be around 3%-4% of the world’s gross domestic product. Therefore, the use of methodologies for corrosion mitigation are extremely important. The approaches used can be passive or active. A passive approach is preventive and may be achieved by emplacing a barrier layer, such as a coating that hinders the contact of the metallic substrate with the aggressive environment. An active approach is generally employed when the corrosion is set in. That seeks to reduce the corrosion rate when the protective barrier is already damaged and the aggressive species (i.e., corrosive agents) are in contact with the metallic substrate. In this case, this is more a remediation methodology than a preventive action, such as the use of coatings. The sol-gel synthesis process, over the past few decades, gained remarkable importance in diverse areas of application. Sol–gel allows the combination of inorganic and organic materials in a single-phase and has led to the development of organic–inorganic hybrid (OIH) coatings for several applications, including for corrosion mitigation. This manuscript succinctly reviews the fundamentals of sol–gel concepts and the parameters that influence the processing techniques. The state-of-the-art of the OIH sol–gel coatings reported in the last few years for corrosion protection, are also assessed. Lastly, a brief perspective on the limitations, standing challenges and future perspectives of the field are critically discussed.

Keywords: sol–gel; coatings; hybrid; corrosion; metallic

1. Introduction

The sol–gel synthesis process is a versatile method used to produce a wide diversity of materials, which range from inorganic glasses to complex organic–inorganic hybrid (OIH) materials [1–7]. Specific types of OIH materials have also been named, either as ORMOSILs (acronym created from organically modified silicates) or OMOCERs (from organically modified ceramics) depending on the precursors employed and on the synthesis route. OIH materials may be described as multicomponent compounds that have at least one of their organic and inorganic components in the sub-micrometric and/or in the nanometric size domain (Figure 1) [8]. The properties of the OIH materials are not the simple addition of the contribution of each individual component; instead, their properties result from the synergy created between the two components (i.e., organic and inorganic). Basically, to synthesize OIH materials through sol–gel method, it is required to introduce molecular precursors which allow the formation of the organic component. This can be achieved by [2,9–12]:

1) Adding organic precursors that are soluble in the reactional media (where hydrolysis/condensation reactions take place), although do not take part in the gel formation. The OIH material obtained
by this route will display an organic component bonded to the inorganic network by van der Waals forces, or ionic or hydrogen bonds.

2) Adding organic alkoxides ($R'M(OR)x$), in which an organic group $R'$ is bonded to the element M and it is not hydrolysable. In this case, the organic and inorganic components establish covalent bonds.

The simple sol–gel processing conditions and the possibility of tuning OIH materials for specific requirements are the main reasons for their development. Moreover, OIH gel materials combine both the advantages of organic polymers (i.e., impact resistance, flexibility and light weight) and the properties of inorganic material components (i.e., chemical resistance, thermal stability and mechanical strength). Therefore, in the last few decades, a remarkable advance regarding OIH materials—controlling structure at a nanometric scale (Figure 1)—was achieved. Controlling at such a scale level allows one to obtain an OIH with certain macroscopic properties that are not present in the individual materials (organic and inorganic components). This allows one to obtain materials with distinctive properties when compared to the separated components. Therefore, OIH sol–gel materials show a huge potential for applications in a wide range of fields as diverse as optical [13], electronics [14], surface treatments [15], construction [16–19], textile [20], energy [21] and health [22], among others. The development of OIH materials, being a multidisciplinary field, involves materials engineering, chemistry, biology, physics, medicine, etc. Moreover, it can be considered that the development of such materials is already impacting people’s lives with significant expression in the medical field [22–25].

**Figure 1.** Materials scale. All the images in this figure were obtained from Wikimedia Commons. Adapted from [26].

OIH materials, compared to pure inorganic glasses, show significant advantages, including: improvement/increase of the flexibility of the silica gel enabling one to produce thick and crack-free films; introduction of reactive functional groups within the OIH network that can be used to anchor molecular recognition groups and allow entrapping higher concentrations of species. The components employed during the synthesis will dictate the properties of the materials. For instance, the use of an inorganic network is limited in terms of implementation and new functionality input. A way to ease the shaping
step and to tailor the bulk properties of the final materials is the introduction of an organic component covalently linked to the network. This can be achieved through the use of an organo-alkoxy silane. The organic component will bring flexibility to the final network modulating either the chemical or the mechanical properties [27]. Organic components can be introduced into the inorganic network as network modifiers or as network formers [2]. The network modifiers contribute to the functionalization of the matrix. For example, some organic precursors, such as methyltriethoxy-silane (MTES), provide flexibility [27,28], while fluoro(triethyl)silane is known for its hydrophobic properties [27,29,30]. The most used network formers are 3-(trimethoxysilyl)propyl-methacrylate (MEMO) [27,31], (3-aminopropyl)triethoxysilane (APTES) [32,33] and (3-glycidoxypropyl)methyltriethoxysilane (GPTMS) [27,34,35]. The mentioned precursors have to be thermally or photo-chemically cured, leading to an organic network linked to an inorganic one. It has also been reported that the addition of organic monomers to a network former contributes to a double reticulation and creates a winding between the organic and inorganic networks [27].

The development of OIH sol–gel coatings, based on siloxanes, for corrosion mitigation, has been widely studied in the last few years [2,31,36–38]. Numerous studies have been conducted since the early 1990s [39,40]. The studies performed showed that siloxanes were effective in mitigating the corrosion processes of different metallic substrates. This development was mainly due to the need for alternative environmentally friend materials and processes to replace the traditional chromium-based pre-treatments. Hexavalent chromium (Cr (VI)) is carcinogenic and shows high environmental toxicity and its use has been forbidden since 2006. However, Cr(VI) based pre-treatments improve the coating adherence to the substrate and are effective corrosion inhibitors [41–43] which make its replacement challenging. The use of the sol–gel method to produce OIH coatings for corrosion mitigation suits the main requirements of what should be an environmentally friendly process (i.e., excludes washing stages; it is a waste-free method) and allows one to obtain coatings with high purity and specific pore volumes and surface areas. Since it is a mild synthesis process (e.g., low temperature synthesis—often close to room temperature), the thermal volatilization and degradation of entrapped species (such as corrosion inhibitors) is reduced. As liquid precursors are used in the sol–gel process, it is possible to cast coatings in and produce thin films without the need for machining or melting [31].

Corrosion is known as one of the most severe complications in modern societies. The corrosion degradation process and subsequent rate of reaction depend on both the physical and chemical properties of the metallic substrates (e.g., steel, aluminum, titanium and respective alloys). Furthermore, the type of corrosion (e.g., pitting, bimetallic, filiform) is also determined by the metallic substrate and environment [44–46]. Aggressive species, such as chloride ions (Cl\(^-\)), O\(_2\), and H\(_2\)O, including the electron transport, play important roles in this process. The deterioration of the metallic substrates may lead to defects that may threaten its performance and lead to earlier failure, which is always linked to high costs, and the resulting losses each year are huge. Several cost-of-corrosion studies have been conducted by several countries (e.g., United States, United Kingdom, Japan, Australia, Kuwait, Germany, Finland, Sweden, India and China). All the studies agreed that the annual corrosion costs ranged from approximately 1% to 5% of the gross domestic product (GDP) of each nation. In 2016, a NACE study estimated a global cost of corrosion at $2.5 trillion annually, equivalent to roughly 3.4% of the global GDP [47]. Moreover, according to 360 Market Updates [48] the global nanostructured coatings and films market was valued at million US$ in 2018, and it is expected that, considering the compound annual growth rate, this market will reach billions of US$ by the end of 2025. The main applications include oil and gas, aerospace and aviation, automotive, textiles and apparel, medical, buildings and consumer electronics industries. Therefore, several approaches are needed for corrosion mitigation. Generally, two approaches are considered; namely: a passive approach that is usually preventive and may be achieved by placing a barrier layer (e.g., coating) which hinders the contact of the metallic substrate with the aggressive environment; and an active approach that is used when the corrosion has already appeared. The damage of the protective layer allows the entrance of corrosive agents that will further attack the metallic substrate. Therefore, an active approach intends to decrease the
corrosion rate and mitigate the development of further corrosion degradation of the metallic substrates. Nevertheless, it is accepted worldwide that only the combination of both methodologies can provide a reliable and durable protection of the metallic substrates against corrosion. Thus, the development of coatings that effectively prevent, mitigate and delay the corrosion process are of extreme importance. A material to be used as a protective coating must include several properties; namely, effective corrosion protection, abrasion and cracking resistance, good adhesion between the metallic surface and the coating and a long-life span. Simple OIH coatings can improve the adherence between the substrate and organic based coatings, for instance. Nevertheless, they behave only as a physical barrier. To obtain OIH with anticorrosive performance, additional functions must be introduced within the OIH network, such as corrosion inhibitors [16,49–51]. The alternatives proposed in the literature include OIH materials containing corrosion inhibitors such as zirconium [33,52–56], titanium [30,57,58] and cerium [50,55,59]. M. Catauro et al. synthesized OIH sol–gel materials based on zirconia (ZrO₂) and poly(ε-caprolactone) to coat pure titanium for implants application [56]. The authors concluded that the OIH films were suitable to coat the metallic implants, to improve their bioactivity and maintain the passivation properties of the metallic substrate. Later, the same authors reported the synthesis of OIH materials by sol–gel method using TiO₂ for the inorganic matrix and poly(ε-caprolactone) as organic component. The material produced was used to improve the performance of Ti6Al4V implants [58]. Most of the data found in the literature indicate that the OIH sol–gel materials show an enormous potential in the field of coatings for corrosion mitigation. Several multifunctional OIH coatings have been reported in the last few years showing promising results, with functions adapted according to each metallic substrate and environment [60–77].

The current review includes four main sections: the first section is dedicated to the concepts of sol–gel process from a historical perspective. The second section describes the fundamentals of the sol–gel method. The third section covers, succinctly, the main progress on the development of OIH sol–gel coatings for corrosion mitigation, including self-healing, anti-fouling and superhydrophobic functions. Finally, the fourth section outlines the challenges and prospects for future research.

2. Sol–gel Process: A Historical Perspective and Applications

This section will briefly focus on the historical perspective of the first industrial interest in sol–gel materials, followed by their commercialization as coatings. A detailed and very complete historical perception on the evolution of OIH material can be found elsewhere [78].

The commercialization of sol–gel coatings appeared about a century after publication of the first scientific papers with Ebelman and Graham’s studies, in 1846, on silica gels [79]. Although noticed as early as 1846, and known to play a part in natural processes (e.g., formation of opal, glasses and ceramics), it was only during the post-World War II period that the solution-sol–gel, commonly known as the sol–gel process, became increasingly exploited for the preparation of glasses and other ceramic materials [80]. Graham (1861) is generally considered as being the founder of colloidal materials science [81]. However, the oldest sols prepared in a lab were made of gold colloidal particles, by Faraday in 1853 [82]. Later, in 1919, W.A. Patrick submitted a patent of a gas mask canister for vapors’ and gases’ adsorption. The innovative part of this patent was the silica-gel made of sodium silicate [83]. In the late 1930s, Gefccken and Dislich from Schott Glaswerke Company, developed the basis of the dip coating process to cover industrial glass with thin oxide layers [84]. The re-introduced attention in the sol–gel process was mainly due to the need for obtaining optical glass components (e.g., lenses, mirrors) at low temperatures without subsequent polishing. Additionally, the opportunity for modifying the materials structures at a nanoscale level (Figure 1) lead to the synthesis of advanced ceramics. From the 1940s until the end of the 1970s, the advances using the sol–gel process were mainly focused on the development of mixed OIH materials [78]. At that time, some labs, such as atomic energy in the United States of America, had already applied the sol–gel route to produce pellets and fuel powders. However, the work developed stayed secret until the 1970s [84]. From the 1980s until nowadays, a huge development in the sol–gel process was achieved. The research conducted allowed them to obtain
OIH materials with applications in a wide range of areas, such as chemical and biosensors [13,85,86], in several transduction modes, from electrochemical [87–91] to optical [13,92–95]; biomaterials for drug delivery [24,96–100]; materials for improving bioactivity and biocompatibility of metallic substrates [101–108]; electronics [14]; environment [109–111]; optics [13,112,113]; medicine [53,114–117]; functional smart coatings [31,38,73,118]; fuel and solar cells [119–122]; and catalysts [123,124] (Figure 2). In 2018, Nourani-Vatani et al. [53] reported that a huge development for hospital equipment, and medical, dental and laboratorial devices using different metallic alloys has been achieved. However, such metallic alloys show some limitations, including low corrosion/wear resistance and unsuitable scratching and hardness properties. Therefore, to solve these drawbacks, several coatings have been proposed [57,101,105,108]. It was also concluded that zirconium-based coatings and OIH materials have been widely studied, as has the application, simultaneously, of polymers and zirconium enhanced several properties; namely, scratching, biocompatibility, bioactivity and hardness [53].

The sol–gel method offers several advantages when compared to traditional synthesis processes [1,36,125–127]; namely, the ease of fabrication and flexibility of the process, the large number of precursor reagents commercially available with tuned functional groups and the low environmental impact. Furthermore, sol–gel also allows for excellent control of the stoichiometry of the precursor; and the incorporation of different components that introduce complementary functions to the material (Figure 2), such as UV protection [128–130], anti-fouling [131,132], anti-reflection [133,134], moisture resistance [135], corrosion protection [15,16,31,38,136–138] and detection of biological components [88,139]—proteins [140] and enzymes [92,141], antibodies [142,143], DNA [95,144,145], polysaccharides [146,147], etc. This feature allows one to obtain, in a simple way, smart and multifunctional materials. Nowadays, the development of OIH sol–gel materials is mostly focused on green [37,49,148], safe, smart [37,149,150] and economic approaches. Ideally, these new materials should be intelligent, with properties such as self-healing abilities [73,151–153] or the capacity to act according to a certain environment/need or property (stimuli-responsive). OIH materials with the ability of reacting to different stimuli, such as mechanical, chemical, optical, electric and thermal ones, in order to mitigate undesired changes, is the focus of most research reported. The search for materials with the capacity to heal, adapt and behave according to each need and environment—multifunctionality—will mark the 21st century achievements.
3. General Concepts of the Sol–gel Process.

The sol–gel synthesis process has been widely reported in the literature [1,2,15,38,154–156]. Therefore, in the present manuscript, only a generic approach on the sol–gel fundamentals will be conducted.

Over the last five decades, an exhaustive development of the synthetic approaches to various oxide materials has been based on the polymerization of metal alkoxides, M(OR), namely, silicon (Si), such as tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS). This process is influenced by several factors; namely: pH, temperature, catalyst, solvent, nature of alkyl group, water to alkoxide molar ratio, etc. Alkoxysilanes generally show a slow kinetic rate when compared to the titanium, aluminum or zirconium alkoxides. This allows a higher chemical control of the process, leading to materials with different properties, such as pore size and distribution, dimension and shape of the particles. Furthermore, silicon shows lower reactivity regarding chelating groups and redox process, which may lead to the formation of sub-products [157].

Table 1 shows chemical structures of the most-used silicon alkoxide precursors in the synthesis of OIH materials. The precursors with polymerizable functional groups, e.g., epoxide (GPTMS), vinyl (VTMS) or methacrylate (MAPTS), besides allowing the formation of an organic network, also contribute to further densification of the OIH material.

| Chemical Name                                      | Abbreviation | Chemical Structures |
|---------------------------------------------------|--------------|--------------------|
| Tetraethoxysilane                                 | TEOS         | ![Chemical Structure](image1) |
| Tetramethylorthosilicate                          | TMOS         | ![Chemical Structure](image2) |
| Methyltriethoxysilane                            | MTES         | ![Chemical Structure](image3) |
| Methyltrimethoxysilane                            | MTMS         | ![Chemical Structure](image4) |
| Vinyltrimethoxysilane                             | VTMS         | ![Chemical Structure](image5) |
| Phenyltrimethoxysilane                            | PTMS         | ![Chemical Structure](image6) |
| 3-Aminopropyltrimethoxysilane                    | APTMS        | ![Chemical Structure](image7) |
| Aminopropyltriethoxysilane                       | APTES        | ![Chemical Structure](image8) |
| N-(2-aminoethyl) 3-aminopropyltrimethoxysilane   | AEAPS        | ![Chemical Structure](image9) |
| 3 - Glycidoxypropyltrimethoxysilane               | GPTMS        | ![Chemical Structure](image10) |
| 3-Methacryloxypropyltrimethoxysilane              | MAPTS        | ![Chemical Structure](image11) |
The chemical reactions involved in the sol–gel process are usually divided into two steps. The first step involves the hydrolysis of metal alkoxides producing hydroxyl groups in the presence of water. The second step is followed by polycondensation of the resulting hydroxyl groups and residual alkoxyl groups, forming a three-dimensional (3D) network, establishing covalent bonds Si–O–Si in the case of silicon alkoxides. Therefore, the alkoxides and esters of inorganic acids are raw materials of utmost importance in the sol–gel technology. In the case of silicon alkoxides, the hydrolysis and condensation reactions may be catalyzed by acids or bases [158]. The structure and morphology of the final material is strongly dependent on the nature of the catalyst and pH of the reaction. The hydrolysis reactions, either catalyzed by acids or bases, are nucleophilic substitution reactions type $S_{N}2$, characterized by a transition state in which the silicon atom is penta-coordinated. The replacement extension of the OR groups by OH groups in the silicon atoms depends on the molar ratio Si/H$_2$O:

$$\text{Si(OR)}_4 + n \text{H}_2\text{O} \rightarrow \text{Si(OR)}_{4-n}(\text{OH})_n + n \text{ROH} \quad (1)$$

For acidic catalysis, the following reaction takes place:

For basic catalysis, the following reaction takes place:

The condensation reaction of Si(OR)$_{4-n}$(OH)$_n$ may also be catalyzed by acids or bases. The reactions for acidic catalysis are:

The reaction mechanism of condensation by acidic catalysis starts with the protonation of the silanol species ending with the formation of a Si–O–Si bond. The reactions for alkaline catalysis are:
For alkaline catalysis, the specie \( \text{HO}^- \) removes the proton from the silanol group, forming a silanolate anion ending with the formation of a Si–O–Si bond. The reactions of alkoxy silanes, in which monomers form polymeric structures by loss of substituents, involve the formation of a colloidal suspension—Sol—followed by the polymerization that will lead to the formation of a 3D structure—gel. For acid catalysis, the alkoxy silane hydrolysis rate shows higher kinetics when compared to basic catalysis. Therefore, the acidic catalysis leads to the formation of a highly branched polymeric structure, while alkaline catalysis leads to colloidal particles with linear chains or a ringed shape. Once the gel is formed, the hybrid network needs to be dried in order to remove the water, alcohol and solvents that are formed during the hydrolysis/condensation reactions.

The drying step has an important role, since, depending on the process used, different materials will be obtained. For instance, if the drying process takes place under normal conditions, a contraction of the gelled network occurs. The obtained dry gel, which is known as xerogel, may shrink between five to ten times in volume when compared to the gel before drying. The shrinkage process includes the transport of the liquid through the pores of structure and contraction of the network \([1,15,38]\). The xerogel is suitable for substrate catalysis, filters, among other applications, mainly due to low porosity and large surface area \([131]\). Several studies have been reported concerning the use of xerogels in the field of filters and membranes \([159]\) and for carbon dioxide capture \([160]\). If the drying of the gel occurs in wet supercritical conditions, the shrinkage will be minimal, and the resulting product is porous and is known as an aerogel \([1,111,161]\). The material is known as a monolith if the dimensions of the gel are greater than scarcely millimeters \([1,162–164]\). In case of the gelation, it takes place by quick evaporation of the solvents; the materials obtained are coatings (Figure 3), films and fibers \([14,154,165]\).

Nevertheless, it should be kept in mind that during the loss of volatile by-products, formed through the hydrolysis and condensation reactions, controlling the sample shrinkage during the 3D network development may be challenging and puzzling \([1,6,7]\). This type of material, composed by organic and inorganic components and known as OIH, is extremely attractive, since it enables an interface between two worlds of chemistry (organic and inorganic), each with unique properties that cannot be found on the individual components.
4. Hybrid Sol–gel Coatings for Corrosion Mitigation

OIHs have numerous remarkable and attractive properties with application in a wide range of fields (Figure 2). However, the huge interest involved in the development of such materials is mainly due to the convenience of the synthesis process. The sol–gel method is a flexible and simple route that allows one to obtain OIH materials in different forms (films, fibers, nanoparticles (NPs), etc.). This synthesis route is exceptionally valuable for the design and production of OIH coatings. Furthermore, sol–gel synthesis route allows one to control, strictly, the precursor stoichiometry, to modify and introduce functional groups or encapsulate different elements. Moreover, it allows one to coat substrates with large surface areas and minimum complex geometries involving simple and inexpensive equipment, as illustrated in Figure 3. It is a process that involves the ability to manipulate nanostructural (Figure 1) properties by controlling the hydrolysis, condensation reactions (Figure 4) and aggregation processes.

![Figure 4](image)

Figure 4. Generic two step reactions involved in the preparation of OIH materials through the sol–gel method using as the network-forming element the Si. R is typically an alkyl group. Adapted from [1].

The properties of OIH sol–gel materials, such as homogeneity, stability and transparency, are largely dominated by the concentrations and types of precursors, the solvent’s nature, the concentrations and types of additives (surfactants, catalysts, etc.), the pH of the reactional media, the heat treatment and the curing time [37,166]. Furthermore, the OIH gel network can be modified with a vast number of dopants [155,167–170] leading to products with singular and extraordinary properties.

The nature of each of the interactions between the organic and inorganic components, within the hybrid networks, was used to establish an OIH classification. The first classification was introduced in 1994 by Sanchez and Ribot [3] and the OIH materials were divided into two classes (class I and II). Later, in 1997, Wojcik and Klein [171] introduced a three class system. OIH materials from class I are the ones where the interactions established between the organic and inorganic components are weak (e.g., hydrogen and ionic bonds, van der Walls bonds, π – π interactions). OIH materials from class II establish strong bonds between the organic and inorganic components, such as covalent bonds. OIH class III are the ones that comprise both the type of bonds established in OIH materials from class I and II.

The requirements for a material to be used as a coating for corrosion mitigation must include effective protection against corrosion, abrasion resistance and a good adhesion between the coating and the substrate surface. The OIHs class II show properties such as high hydrophobicity, good corrosion protection, low dielectric constants or good scratch resistance [12,31]. Therefore, these chemical and physical properties make the OIH class II the ones more suitable to mitigate corrosion/oxidation of the metallic substrates. OIH class II can be easily prepared by the sol–gel process in which the alkoxyisilane precursor, generally a trialkoxyisilane, has an alkyl group bonded to the silicon atom producing monomers in R’Si(OR)₃ in which R’ may be H, CH₃, CH₂CH₃ or an aromatic group (Table 1). This alkyl group, by establishing a bond C–Si does not react (e.g., hydrolysis/condensation reactions) and remains covalently bonded to the silicon groups, through the C–Si bond, making part of the
final material structure (Figure 4). These materials, known as polysilsesquioxane (R’SiO$_{1.5}$) [172–174] have desirable properties, such as good hydrophobicity and chemical and thermal stability. The organic groups R’ are network modifiers and reduce the functionality of the silicon atoms, turning the silica network less brittle and rigid [175]. Another example of this type of material consists of the incorporation of a polydimethylsiloxane (PDMS) network linked to the SiO$_2$ network by the co-condensation of PDMS oligomers in a sol–gel reaction [176,177]. Monomers R’Si(OR)$_3$, in which R’ is an organic reactive group, such as amine, isocyanate, vinyl or epoxide (Table 1), may be used to obtain polysilsesquioxanes by sol–gel. The organic groups, through the combination of suitable monomers, may allow the formation of bridges between the silicate groups [175]. Examples of these types of products were reported by different authors [16,17,162,164]. In the last fifteen years, several review articles have been published in the design and application of OIH materials, and mostly were approached from the point of view of materials [2,3,12,27,36,112,148,178–182]. Table 2 shows the most relevant review manuscripts published since 2016 focused on OIH sol–gel materials.

| Year | Reference | Discussed subject matter |
|------|-----------|--------------------------|
| 2016 | [183]     | Principles and morphologies of microcapsules, purpose of microencapsulation, physical, and chemical techniques and healing mechanisms for the coating industry were debated. |
|      | [184]     | The progress made in the synthesis of several sol–gel-derived materials was reviewed. The main achievements in the field of anticorrosion coatings were also debated. |
|      | [37]      | Summary of the main research achievements in the development, of OIH sol–gel coatings for corrosion mitigation of steel and aluminum substrates. |
|      | [185]     | The general features of OIH coatings, and recent developments were summarized. Summary of the latest achievements and strategies for the sol–gel process parameters and other factors that influence the corrosion properties of the OIH coatings for corrosion protection of aluminum-based alloys. |
|      | [137]     | Overview of sol–gel technology where the fabric functions that can be achieved by this technology are debated including anticorrosion coatings. |
| 2017 | [186]     | Advances in smart coatings, including OIH coatings, with response to different stimuli and damage modes were reviewed. Emphasis was on corrosion sensing, self-cleaning, anti-fouling, and self-healing polymeric coating systems. |
|      | [187]     | Recent applications using PDMS polymers for anticorrosion, anti-biofouling, anti-icing, flame-resistant and self-cleaning, anti-reflection were reviewed. |
|      | [188]     | Overview of the superhydrophobic coatings (including OIH sol–gel) reported in literature for steel protection and their performances. |
| 2018 | [138]     | Different solutions for slow down the corrosion processes of metallic substrates by using the oxides and doped oxides obtained by the sol–gel method were discussed. Analysis of some of the most representative examples of the application of electrochemical techniques such as EIS, PDP, SVET, SIET, SKP and LEIS to determine the exact mechanism of protection offered by sol–gel coatings on metallic substrates. Description of the historical perception of OIH material science. The major periods linked to the genesis of OIH materials were discussed. |
|      | [189]     | The main aspects of the use of silicon polymers for coatings were debated. The advantages and disadvantages of these materials, and the processing methods developed were discussed. |

Table 2 shows that numerous OIH sol–gel coatings for corrosion applications were developed [30,50,137,191–197]. The number of reviews reported, only since 2016, clearly indicates that this field is still under development and is far from reach a matured stage. Several OIHs for corrosion mitigation have been proposed for a wide range of metallic substrates, including aluminum and its alloys [30,63,74,137,198], carbon steel [193], stainless steel [196,199–201] and galvanized steel [16,17,202–204]. Copper [205–207] and magnesium [208–214] based alloys are other types of substrates in which OIH sol–gel coatings were used. Figueira et al. [31] summarized the application of OIH (class II) siloxane-based coatings on different types of metallic substrates and respective alloys (steel,
aluminum, copper, magnesium and zinc alloys) and the main precursors employed in OIH coatings synthesis. The authors showed that most of the OIH coatings developed were for aluminum-based alloys followed by iron-based alloys. Nowadays, the tendency reported for aluminum-based alloys seems to be maintained [215–220]. Moreover, in the last decade, considerable attention has been given to the development of advanced and multifunctional OIH sol–gel coating materials. Impressive advances have been reported concerning the use of carriers [49,51,149,221–224] loaded with functional abilities (e.g., self-healing [61,73,152,213], anti-fouling [132] and hydrophobicity [30,225]).

4.1. Sol–gel Coatings with Self-healing Function

In the last few years, the interest in developing materials with self-healing ability led to outstanding developments [64,152,226–230]. Self-healing ability can be achieved at different levels of the coating system and by different strategies [231] and is known as the ability of a coating, in a certain environment, repair damaged areas due to external factors (Figure 5). According to Hia et al. [232] self-healing coatings may be classified into two types: intrinsic and extrinsic. Intrinsic coatings are the ones with a latent self-healing functionality and have the ability of heal the coatings matrices by themselves. Extrinsic coatings have a healing agent microencapsulated and embedded within the coating matrix. In this case, when the microcapsules are ruptured by damage, pH or another trigger, the healing agent is released and seals the damaged region, and the healing reaction takes place.

![Figure 5](image_url). Schematic of corrosion self-healing mechanism with an OIH sol–gel coating containing nanocontainers loaded with corrosion inhibitors. Adapted from [37,233].

Strategies such as the addition of polymerizable agents [69,209] to restore/heal the damage in a polymeric coating or the inclusion of corrosion inhibitors (Figure 5) [50,153,221,234] to stop the damage spread have been reported. Metals such as cerium [50,59,200,220,235–238], lanthanum [239–241] or zirconium [33,53] have been incorporated in OIH sol–gel coatings in order to stop corrosion propagation [234,236,237,242,243]. Studies based on OIH coatings doped with cerium inhibitors have been reported since 2002 [235,244]. However, this review will focus only on the publications performed after 2015. Concerning the use of cerium as a corrosion inhibitor, the authors L.R.V. et al. [50] in 2017 performed a comparative study on the effect of CeO$_2$ NPs and Ce(III) ions as corrosion inhibitors in silica-alumina OIH sol–gel coatings. The coatings doped with cerium nitrate (Ce(NO$_3$)$_3$) showed poorer corrosion behavior when compared to CeO$_2$ NPs. The authors attributed this difference to the leaching...
out of Ce(III) ions in case of coatings doped with Ce(NO$_3$)$_3$. This behavior was not reported for coatings doped with CeO$_2$ NPs. It was also concluded that the coatings doped with CeO$_2$ NPs were more “compact,” minimizing the electrolyte ingress and therefore providing improved protection. U. Tiringer et al. [220] produced OIH sol–gel coatings, based on TEOS and GPTMS precursors and containing SiO$_2$ particles and Ce(NO$_3$)$_3$ for corrosion mitigation of aluminum alloy AA7075 in the presence of Cl$^-$. The authors concluded that the curing procedure affected the coating properties obtaining coatings with lower roughness, reduced thickness and higher density by using a curing heating ramp. The incorporation of Ce(NO$_3$)$_3$ increased the roughness and thickness linked to a network with higher porosity. The authors showed that the porosity allowed the release and migration of the incorporated Ce(III) ions. The electrochemical data indicated that the coatings doped with Ce(NO$_3$)$_3$ and cured with heating ramp exhibited improved corrosion properties. Later, in 2019 the same authors [238], reported the synthesis of OIH sol–gel coatings based on the same precursors also doped and undoped with Ce(NO$_3$)$_3$. The effects of curing temperature and the addition of Ce(NO$_3$)$_3$ on the degree of polycondensation of the OIH sols were studied. It was concluded that the addition of Ce(NO$_3$)$_3$ did not affect the viscosity of sols and improved their thermal stability. Furthermore, the authors revealed that the addition of Ce(NO$_3$)$_3$ acted as an initiator, stimulating the polycondensation reaction at lower temperatures. Earlier this year [59], T.T. Thai, et al. developed OIH sol–gel coatings doped with Ce(III) ions by using montmorillonite as container. The electrochemical studies showed that the coatings were effective at protecting the metallic substrate. At a low concentration of cerium-modified clay particles (0.5% wt.), the Ce (III) played a role as effective cathodic inhibitor of the metallic substrate. The leached cerium rate obtained was about 70%, and the authors showed that it was from the Ce(III) ions that were deposited, in the beginning, on the external layer of the clay platelets. In the end, it was concluded that the Ce(III) ions at the external layer of clay platelets induced the formation of Ce(OH)$_2$, strengthening the corrosion protection of the OIH coating [59].

In the case of using lanthanum as a corrosion inhibitor, P. Balan et al. [240] in 2016 reported a study on the electrochemical behavior of modified silane films with lanthanum triflate salt (LTS) and/or silica NPs. The incorporation of LTS or silica NPs enhanced the anti-corrosion behavior of the silane films when compared to pure films. The films modified by both LTS and silica NPs showed improved corrosion protection. The authors also concluded that the direct addition LTS could compromise the coating barrier properties and the stability of the silane solution. These limitations were improved by incorporating La$^{3+}$ cations in amorphous silica NPs before being embedded into the silane film. Two years later, J. Peña-Poza et al. [241] studied TEOS sol–gel based coatings doped with lanthanum acetate/nitrate on different metallic substrates (i.e., copper, bronze, lead and steel). The authors concluded that La$_2$O$_3$ was adequate to incorporate La$^{3+}$ ions within the silica matrix. Furthermore, the produced coatings mitigated the corrosion process on copper, bronze and lead, while steel substrates required thicker coatings.

Ideally, the addition of species (e.g., corrosion inhibitors and polymerizable species) to improve the OIH coating’s performance must be incorporated within the coating matrix and released when required, i.e., when corrosion the process initiates, in order to delay further corrosion development. It has been reported in different studies that the direct incorporation of these species may interfere with the curing of the coating material and compromise its physico-chemical performances [16,203,245]. Therefore, the selection of suitable carriers/nanocontainers, to ensure their release in response to a trigger (stimulus-responsive), is of extreme importance [67,151,228]. The trigger which can be physical or chemical (i.e., crack propagation, the presence of moisture, pH, aggressive species) [227,235,246–250]. Furthermore, these nanocontainers must be able to stock the required species in sufficient amounts and be compatible with the coating itself. The most commonly used reservoirs reported in the literature include urea-formaldehyde capsules [246–249], hydroxyapatite particles [57,251], chitosan [243,252] and halloysite nanotubes [213,221]. Several OIH sol–gel coatings have been reported as smart with self-healing abilities, such as the remarkable works reported by the M.G.S. Ferreira group [63,76,149,150,253–258] and Adsul et al. [66,213,259].
Adsul et al. [66,213] studied the effect of loading cationic corrosion inhibitors (Ce$^{3+}$/Zr$^{4+}$) into halloysite nanotubes, which were afterwards incorporated within an OIH sol–gel matrix and deposited on magnesium alloy substrates. The authors concluded the Ce$^{3+}$/Zr$^{4+}$ loaded halloysite nanotubes dispersed within the OIH coating provided suitable corrosion protection of the substrate when exposed to 3.5% NaCl. The healing properties were confirmed through weight loss and electrochemical techniques. The same research group [259] also studied the incorporation of the same corrosion inhibitors into aluminum pillared montmorillonite clay. The montmorillonite clay was dispersed as received within the matrix sol–gel coatings. The coatings mitigated the corrosion process during the beginning of exposure to aggressive environment. Another coating in which the pillared clay was modified, by evaporation of a mixture of corrosion inhibitor and pillared montmorillonite, provided improved corrosion protection for higher exposure periods in the same environment. This was shown by electrochemical and weight loss measurements. However, by increasing the coating exposure time in the aggressive environment, the coating suffered deterioration. It was also proven that the coatings provided autonomous healing in case of long-time exposure.

The self-healing mechanism in corrosion mitigation may be assessed and validated by several electrochemical tools. The most common techniques reported to assess the self-healing and corrosion inhibition of such materials are scanning vibrating electrode technique (SVET), scanning ion selective electrode technique (SIET) and localized impedance spectroscopy (LEIS) [231].

4.2. Sol–gel Coatings with Anti-Fouling Function

Anti-fouling is another important function to enhance the corrosion protection of a coating. Coatings designed for this purpose are generally based on dense organic matrices, containing wide-spectrum biocides such as tributyltin and tributyltin oxide. These biocides are one of the major contaminants in marine and freshwater ecosystems [260], and nowadays their use is forbidden. Therefore, there is an emergent interest in develop new coatings with controlled release of benign biocides [141,261–266]. The use of nanocontainers loaded with biocides is considered a very attractive methodology, since a controlled release can minimize the environmental impact.

In the last 20 years, anti-fouling coatings have been extensively studied [110,141,261,267–274], including sol–gel coatings with anti-fouling properties [131,132,262,275]. Although many approaches and routes have been proposed [131,132,231,262–264,276–279], there is still an absence of long-term and effective solutions. Generally, two corrosion mechanisms in the marine environment are considered; i.e., microbiologically influenced corrosion (MIC) and marine bio-fouling. Y. Li and C. Ning [280] published a review focused on the research progress regarding these two mechanisms. The authors concluded that MIC and bio-fouling are prevented by the control of the microorganisms’ activities in biofilms, their adhesion and their formation of biofilms. It was also concluded that the performance of antifouling coatings has been improved by the modification of self-polishing copolymers and the development of degradable polymers. Conducting polymers were also developed and introduced to mitigate corrosion and biofouling.

A wide range of encapsulated agents for fouling mitigation were proposed and assessed, including enzymes [88,141,281–283], ZnO$_2$ NPs [284], silver and benzalkonium chloride [265], zinc pyrithione [264] and chlorhexidine [275]. The encapsulation of enzymes showed auspicious results [141,281–283]. For example, M. Meißler, et al. [283] reported the combination of a titanium binding peptide to a linear peptide-block-poly(ethylene glycol). The adsorption function of the peptide segments within peptide-PEG conjugates was weakened by enzymatic proteolysis. It was concluded that the adsorption properties related to the titanium substrate were fully suppressed, showing potential for antifouling surfaces in the biomedical field. Coatings combining both anti-fouling and anti-corrosion functions have also been reported [265,285–287]. Arukalam et al., for instance, prepared perfluorodecyltrichlorosilane-based poly(dimethylsiloxane)-ZnO coatings for fouling and corrosion mitigation. The authors chose the ZnO NPs to study the influences of the particles’ nature: the hydrophilic and anti-fouling properties. The efficacy of the produced coatings was assessed, and it
was concluded that they were promising for such application. E. Wallström et al. [264] reported an auspicious route to introduce anti-fouling functionalities within a coating, wherein it was shown that the use of zinc pyrithione reduced the release rate of the biocide when compared to the release rate for the free biocide particles in demineralised water. The authors also showed that the water uptake in the paint had a major impact on the biocide release and was dependent on a number of properties, such as the binder system, pigmentation, the amount of gel and the active component included. In the end, the authors concluded that to produce formulations without the use of bio-accumulative compounds and to minimize the biocide component, it was necessary to take into account gel composition, paint formulation and water exposure. Oldani et al. [132] in 2016, reported a study where the use of OIH sol–gel coatings was promising for producing coatings for fouling mitigation. The authors combined a commercial a,v-substituted perfluoropolyether with TEOS for deposition on stainless steel substrates. It was concluded that to obtain a suitable balance between the hydrophobic properties and the film formation, the amount of polymer ranged between 70 and 80 wt.% The OIH coatings reported showed a water contact angle (WCA) between 130° and 140° and good chemical resistance. M. Barletta et al. [261] developed a promising and effective “biocide-free” antifouling coating system. The proposed system involved the use of a polyester-modified, OH-rich polysiloxane that was cured through reactions with different commercially isocyanate hardeners. The hydrophilic and hydrophobic domains were introduced within the system on the curing agent using PEG-olate alkyl and cyclohexyl substituents, respectively. It was concluded that all the samples showed improved results when compared to samples coated with a traditional paint. S. Holberg et al. [285] recently reported the synthesis of a hydrophilic, biocide-free fouling-release coating. The authors prepared coatings from commercial precursors by dispersing a polydimethyl siloxane (silicone,PDMS)-polyethylene glycol triblock-copolymer in PDMS (PEG-PDMS-PEG). It was shown that the fouling growth in a *Pseudomonas aeruginosa* culture test was reduced compared to PDMS without PEG or to steel.

### 4.3. Coatings with Superhydrophobic Function

Micro- and nanopores in the coatings may lead to the entrance of water and aggressive species, causing coating blistering; then peeling; and subsequently, corrosion of the metallic substrates. Therefore, an interesting approach to prevent corrosion is the development of superhydrophobic surfaces. A coating shows hydrophobic properties when the WCA on a surface is above 90°. In the case of superhydrophobic coatings, they require a WCA above 150° and a contact angle hysteresis (CAH) lower than 10° [288,289]. CAH is expressed as the difference between the advancing and the receding WCA of a water droplet that expands or shrinks on the surface [290]. Additionally, these coatings should show a roll-off angle lower than 10°. According to K.K. Varanasi et al., the roll-off angle is defined as the lowest angle that a surface needs to be inclined at before the water droplet slide or rolls off it [291]. The reduction of the WCA and contact time on the superhydrophobic surfaces mitigate the interaction between the metallic substrates and the aqueous corrosive species. This behavior allows to enhance the corrosion protection of the substrates by indirectly avoiding the contact between the metallic surface and the aggressive species [292–295]. In the last few years, the literature reported on this type of coatings increased notably [60,291–293,296–299]. Numerous techniques and methods have been used in the development of superhydrophobic surfaces [300–302], and the sol–gel process, as the versatile method that it is, was no exception [294,299,303–307]. Recently, a very detailed and comprehensive review, focused on the latest developments of superhydrophobic coatings for corrosion mitigation, has been published [308]. The challenges and limitations of the synthesis of stable superhydrophobic coatings were also included and discussed. One of the main advantages of superhydrophobic coatings is that these types of materials may include other properties, such as anti-fouling [276], anti-icing [309] and bio-corrosion [231]. According to a review published by Montemor [231] in 2014, several reported encapsulation-based strategies seem to be promising; however, only a few studies were reported which validated the proposed strategies regarding the corrosion protection behavior [310–312]. However,
important advances and developments on superhydrophobic surfaces have been achieved in the last five years [60,132,136,217,225,240,292,294,297,300,313].

OIH sol–gel coatings with superhydrophobic properties for corrosion mitigation have been reported for different substrates, such as aluminum [295,311,314–318], copper [225,319], magnesium [320], mild steel [321,322] and stainless steel [323]. Generally, OIH sol–gel coatings show improved UV and thermal stability when compared to organic coatings due to the high strength of the Si–O bond. Most of the developments were for application in aluminum substrates. Lee and Hwang [314] reported the development of a superhydrophobic surface for Al/Si alloy by sol–gel process. The authors fabricated a silica gel layer from the Si content of the alloy itself without the need for treatment with high temperatures with an average WCA of 166.04°. By removing one step (temperature treatment), the fabrication of such coatings becomes easier, lower in cost and enabling of its application in industry. The superhydrophobic properties can be obtained by different encapsulation routes. Wang et al. reported the storage of Ca(OH)₂ inside microcapsules and concluded that these show appropriate superhydrophobic performances, including regenerative ability [324]. Porous silica capsules were also reported and tested by several authors [305,310,325–328]. These proved to be efficient in the development of superhydrophobic surfaces for diverse applications. Caldarelli et al. [225] reported the synthesis of a OIH superhydrophobic sol–gel coating for copper metallic substrates. The sandblasted copper substrates were coated with an alcoholic alumina sol followed by thermal annealing that was coated afterwards with a fluoroalkysilane solution. The two-step coating deposition was performed using dip-coating technique. The authors obtained a superhydrophobic coating, and for a WCA of 180° the thermal treatment should be between 200 °C and 250 °C. Zhang et al. [322], in 2016, produced superhydrophobic films to coat mild steel substrates. The authors obtained films by using a two-step route that included the electrodeposition of silica film followed by modification with a long alkyl-chained organic silane (dodecyltrimethoxysilane). It was concluded that the produced coatings showed improved corrosion resistance compared to conventional dodecyltrimethoxysilane-silanized coatings in aggressive environments.

A. Fihri et al. [188] published a review paper where the superhydrophobic coatings reported in the literature, until 2017, for steel protection, and their performances, were debated. The diverse models used to assess the wettability of a surface, and the approaches used to produce superhydrophobic coatings and their impacts on the corrosion mitigation of steel, were also revised. The authors concluded that remarkable advances in the development of superhydrophobic coatings have been achieved during the last two decades. However, most of the advances reported in the literature for the fabrication of such coatings still face many challenges for large-scale deployment. The main challenges identified were the short service life; low curing temperature and adhesion performance; low mechanical robustness; and the high costs involved. Therefore, the authors believe that due to the constraints still present in the development of such coatings, the research will progress towards overcoming these drawbacks in this field.

Superhydrophobicity, besides improving anti-fouling function, allows the encapsulation of active agents, as mentioned earlier. Therefore, the surface finishing can deliver both functionalities [231]. The sol–gel method and the use of silica particles are easy-going routes for achieving anti-fouling, anticorrosion and superhydrophobic coatings.

5. Challenges and Prospects for the Future Research

Nowadays, many of the effective coatings for corrosion protection represent dangers to the environment. Therefore, the key is the development of innovative materials with improved performances and promoting a sustainable environment at the same time.
The corrosion mitigation/prevention of metallic substrates is not only an engineering effort, but also a fundamental scientific difficulty. Ideally, an anticorrosion coating should be designed to be stimulus-responsive, multifunctional, resistant and durable in a wide range of applications. Coatings for corrosion mitigation are normally exposed to complex environments. Therefore, studies on how the different aggressive species (i.e., Cl\(^-\)) and water behave and react within the coating at atomic and nanoscales are needed.

The opportunity of hosting different functionalities broadens the range of applications for OIH sol–gel materials, which can be functionalized with carriers loaded with different agents. However, the development of this type of material requires multidisciplinary collaboration, including materials science, biology and polymer chemistry. Ideas for the encapsulation of anti-fouling species have been transferred from the biological and medical fields. The OIH sol–gel materials’ features allow one to obtain multifunctional coatings, such as self-responsive materials with anti-fouling, anticorrosion and superhydrophobic functions within the same matrix. The existent literature clearly shows that the distinctive properties of the OIH sol–gel materials can be successfully employed for the development of coatings for corrosion mitigation of different metallic surfaces in challenging environments. However, further studies should be performed using different corrosion inhibitors and different trigger stimuli. Stability and long-term healing capacity research should also be considered in depth, since these agents should maintain their function abilities for an extended period (i.e. at least 20 years). Additionally, multi-damaging and the size of the area damaged may be a drawback for these coatings and should be further investigated. On the other hand, sustainability at a large scale, toxicity and the effects of inherent properties of OIH coatings remain only vaguely explored. Although several OIH coatings for corrosion mitigation have been subjected to intensive research, it seems that further investigations are still necessary for both fundamental and applied aspects. The synthesis of OIH multifunctional coatings (e.g., anticorrosion properties, high hydrophobicity, suitable adhesion performance, self-healing abilities) with extended service lives—highly required in order to develop commercial scale products—has not been accomplished yet.

Smart coatings with self-healing functions and stimulus-responsiveness are potentially the future of developments. Self-healing by the incorporation of responsive additives within the OIH coating materials enables, due to external stimulus (e.g., pH, the presence of Cl\(^-\), UV, temperature and/or humidity), the restoration of the material structure and recover the integrity of the protective coating. Hence, suppressing the beginning of corrosion process and increasing the service life of the metallic materials. Additionally, the incorporation of inhibitors that can mitigate and control the corrosive substances ingress will provide extra protection together with the coating structure restored. This direction in the development of smart coatings for corrosion mitigation will for certain mark the 21st century achievements.

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Abbreviations

3-D  Three-dimensional  
EIS  Electrochemical impedance spectroscopy  
CAH  Contact angle hysteresis  
CNT  Carbon nanotubes  
DNA  Deoxyribonucleic acid  
GDP  Gross domestic product  
LEIS  Localized electrochemical impedance spectroscopy  
LTS  Lanthanum triflate salt  
MIC  Microbiologically influenced corrosion  
MTES  Methyltriethoxy-silane  
NPs  Nanoparticles  
OIH  Organic-inorganic hybrid  
PDP  Potentiodynamic polarization  
QDs  Quantum dots  
SIET  Scanning ion-selective electrode technique  
SVET  Scanning vibrating electrode technique  
SKP  Scanning Kelvin probe  
TEOS  Tetraethoxysilane  
WCA  Water contact angle

References

1. Brinker, C.J.; Scherer, G.W. Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing; Academic Press: Boston, MA, USA, 1990; ISBN 0-12-134970-5.
2. Sanchez, C.; Belleville, P.; Popall, M.; Nicole, L. Hybrid materials themed issue. Chem. Soc. Rev. 2011, 40, 453–1152.
3. Sanchez, C.; Ribot, F. Design of hybrid organic-inorganic materials synthesized via sol-gel chemistry. New J. Chem. 1994, 18, 1007–1047.
4. Judeinstein, P.; Sanchez, C. Hybrid organic–inorganic materials: A land of multidisciplinarity. J. Mater. Chem. 1996, 6, 511–525. [CrossRef]
5. Sanchez, C.; Juliá, B.; Belleville, P.; Popall, M. Applications of hybrid organic–inorganic nanocomposites. J. Mater. Chem. 2005, 15, 3559–3592. [CrossRef]
6. Jones, J.R. Review of bioactive glass: From Hench to hybrids. Acta Biomater. 2013, 9, 4457–4486. [CrossRef]
7. Hench, L.L.; West, J.K. The sol-gel process. Chem. Rev. 1990, 90, 33–72. [CrossRef]
8. CRC Concise Encyclopedia of Nanotechnology—CRC Press Book. Available online: https://www.crcpress.com/CRC-Concise-Encyclopedia-of-Nanotechnology/Kharisov-Kharissova-Ortiz-Mendez/p/book/9781466580343 (accessed on 4 March 2020).
9. Zheludkevich, M.L.; Salvado, I.M.; Ferreira, M.G.S. Sol–gel coatings for corrosion protection of metals. J. Mater. Chem. 2005, 15, 5099. [CrossRef]
10. Pierre, A.C. Applications of Sol-Gel Processing. In Introduction to Sol-Gel Processing; The Kluwer International Series in Sol-Gel Processing: Technology and Applications; Springer: New York, NY, USA, 1998; pp. 347–386. ISBN 978-0-7923-8121-1.
11. Bervenutti, E.V.; Moro, C.C.; Costa, T.M.H.; Gallas, M.R. Materiais híbridos à base de silica obtidos pelo método sol-gel. Quimica Nova 2009, 32, 1926–1933. [CrossRef]
12. José, N.M.; de Prado, L.A.S.A. Materiais Híbridos Orgânico-Inorgânicos: Preparação e Algumas Aplicações. Quimica Nova 2005, 28, 281–288. [CrossRef]
13. Nedeljko, P.; Turel, M.; Lobnik, A. Hybrid sol-gel based sensor layers for optical determination of biogenic amines. Sens. Actuators B Chem. 2017, 246, 1066–1073. [CrossRef]
14. Mensing, J.P.; Wisitsoraat, A.; Tuantranont, A.; Kerdcharoen, T. Inkjet-printed sol–gel films containing metal phthalocyanines/porphyrins for opto-electronic nose applications. Sens. Actuators B Chem. 2013, 176, 428–436. [CrossRef]
15. Figueira, R.B.; Silva, C.J.R. Hybrid Sol-Gel Coatings for Surface Protection. In *World Scientific Reference of Hybrid Materials*; World Scientific Series in Nanoscience and Nanotechnology; World Scientific: Singapore, 2019; pp. 145–192. ISBN 978-981-327-055-8.
16. Figueira, R.B.; Silva, C.J.; Pereira, E.V.; Salta, M.M. Ureasilicate Hybrid Coatings for Corrosion Protection of Galvanized Steel in Cementitious Media. *J. Electrochem. Soc.* 2013, 160, C467–C479. [CrossRef]
17. Figueira, R.B.; Silva, C.J.; Pereira, E.V.; Salta, M.M. Alcohol-Aminosilicate Hybrid Coatings for Corrosion Protection of Galvanized Steel in Mortar. *J. Electrochem. Soc.* 2014, 161, C349–C362. [CrossRef]
18. Figueira, R.B.; Silva, C.J.R.; Pereira, E.V. Hot-dip galvanized steel dip-coated with ureasilicate hybrid in simulated concrete pore solution: Assessment of coating morphology and corrosion protection efficiency. *Prog. Org. Coat.* 2015, 88, 245–255. [CrossRef]
19. Figueira, R.B.; Silva, C.J.; Pereira, E.V. Ureasilicate Hybrid Coatings for Corrosion Protection of Galvanized Steel in Chloride-Contaminated Simulated Concrete Pore Solution. *J. Electrochem. Soc.* 2015, 162, C666–C676. [CrossRef]
20. Ismail, W.N.W. Sol–gel technology for innovative fabric finishing—A Review. *J. Sol.–Gel Sci. Technol.* 2016, 78, 698–707. [CrossRef]
21. Akkalouch, M.; Calleja, A.; Granados, X.; Ricart, S.; Boffa, V.; Ricci, F.; Puig, T.; Obradors, X. Hybrid sol–gel layers containing CeO$_2$ nanoparticles as UV-protection of plastic lenses for concentrated photovoltaics. *Sol. Energy Mater. Sol. Cells* 2014, 120 Pt. A, 175–182. [CrossRef]
22. Rathinamala, I.; Jeyakumaran, N.; Prithivikumaran, N. Sol-gel assisted spin coated CdS/PS electrode based glucose biosensor. *Vacuum* 2019, 161, 291–296. [CrossRef]
23. Chen, Y. Synthesis of Hollow Mesoporous Silica Nanoparticles by Silica-Etching Chemistry for Biomedical Applications. In *Design, Synthesis, Multifunctionalization and Biomedical Applications of Multifunctional Mesoporous silica-Based Drug Delivery Nanosystems*; Springer Theses; Springer: Berlin/Heidelberg, Germany, 2016; pp. 31–46. ISBN 978-3-662-48620-7.
24. Razo-Medina, D.A.; Trejo-Durán, M.; Alvarado-Méndez, E. Cholesterol biosensor based on a plastic optical fibre with sol–gel: Structural analysis and sensing properties. *J. Mol. Opt.* 2018, 65, 348–352. [CrossRef]
25. Panneerselvam, S.; Choi, S. Nanoinformatics: Emerging Databases and Available Tools. *Int. J. Mol. Sci.* 2014, 15, 7158–7182. [CrossRef] [PubMed]
26. Le Bail, N.; Benayoun, S.; Toury, B. Mechanical properties of sol–gel coatings on polycarbonate: A review. *J. Sol.–Gel Sci. Technol.* 2015, 75, 710–719. [CrossRef]
27. Lionti, K.; Toury, B.; Boissière, C.; Benayoun, S.; Miele, P. Hybrid silica coatings on polycarbonate: Enhanced properties. *J. Sol.–Gel Sci. Technol.* 2013, 65, 52–60. [CrossRef]
28. Çakır, M. Investigation of Coating Performance of UV-Curable Hybrid Polymers Containing 1H,1H,2H,2H-Perfluorooctyltrioethoxysilane Coated on Aluminum Substrates. *Coatings* 2017, 7, 37. [CrossRef]
29. Rivero, P.J.; Maeztu, J.D.; Berlanga, C.; Miguel, A.; Palacio, J.F.; Rodriguez, R. Hydrophobic and Corrosion Behavior of Sol-Gel Hybrid Coatings Based on the Combination of TiO$_2$ NPs and Fluorinated Chains for Aluminum Alloys Protection. *Metals* 2018, 8, 1076. [CrossRef]
30. Figueira, R.B.; Silva, C.J.R.; Pereira, E.V. Organic–inorganic hybrid sol–gel coatings for metal corrosion protection: A review of recent progress. *J. Coat. Technol. Res.* 2015, 12, 1–35. [CrossRef]
31. Lei, L.; Cao, Z.; Xie, Q.; Fu, Y.; Tan, Y.; Ma, M.; Yao, S. One-pot electrodeposition of 3-aminopropyltriethoxysilane-chitosan hybrid gel film to immobilize glucose oxidase for biosensing. *Sens. Actuators B Chem.* 2011, 157, 282–289. [CrossRef]
32. Yu, M.; Xue, B.; Liu, J.; Li, S.; Zhang, Y. Electrophoretic deposition of hybrid coatings on aluminum alloy by combining 3-aminopropyltrimethoxysilane to silicon–zirconium sol solutions for corrosion protection. *Thin Solid Films.* 2015, 590, 33–39. [CrossRef]
33. Kim, E.K.; Won, J.; Do, J.; Kim, S.D.; Kang, Y.S. Effects of silica nanoparticle and GPTMS addition on TEOS-based stone consolidants. *J. Cult. Herit.* 2009, 10, 214–221. [CrossRef]
34. Mrad, M.; Montemor, M.F.; Dhouibi, L.; Triki, E. Deposition of hybrid 3-GPTMS’s film on AA2024-T3: Dependence of film morphology and protective performance on coating conditions. *Prog. Org. Coat.* 2012, 73, 264–271. [CrossRef]
36. Sanchez, C.; Rozes, L.; Ribot, F.; Laberty-Robert, C.; Grosso, D.; Sassoye, C.; Boissiere, C.; Nicole, L. “Chimie douce”: A land of opportunities for the designed construction of functional inorganic and hybrid organic-inorganic nanomaterials. *Comptes Rendus Chim.* **2010**, *13*, 3–39. [CrossRef]

37. Figueira, R.B.; Fontinha, I.R.; Silva, C.J.R.; Pereira, E.V. Hybrid Sol-Gel Coatings: Smart and Green Materials for Corrosion Mitigation. *Coatings* **2016**, *6*, 12. [CrossRef]

38. Figueira, R.B.; Silva, C.J.R. Application of Sol–Gel Method to Synthesize Organic–Inorganic Hybrid Coatings to Minimize Corrosion in Metallic Substrates. In *Hybrid Organic–Inorganic Interfaces*; John Wiley & Sons, Ltd.: Hoboken, NJ, USA, 2017; pp. 355–412. ISBN 978-3-527-80713-0.

39. Van Ooij, W.J.; Sabata, A. Characterization of films of organofunctional silanes by TOF SIMS and XPS. *J. Adhes. Sci. Technol.* **1991**, *5*, 843–863. [CrossRef]

40. Verma, a.R.B.; van Ooij, W.J. High-temperature batch hot-dip galvanizing. Part 1. General description of coatings formed at 560 °C. *Surf. Coat. Technol.* **1997**, *89*, 132–142. [CrossRef]

41. Fedrizzi, L.; Terryn, H.; Simoes, A. *Innovative Pre-Treatment Techniques to Prevent Corrosion of Metallic Surfaces*; Elsevier: Amsterdam, The Netherlands, 2014; ISBN 978-1-84569-368-8.

42. Pehkonen, S.O.; Yuan, S. *Tailored Thin Coatings for Corrosion Inhibition Using a Molecular Approach*; Academic Press: Cambridge, MA, USA, 2018; ISBN 978-0-12-813585-3.

43. Ferreira, M.G.S.; Duarte, R.G.; Montemor, M.F.; Simões, A.M.P. Silanes and rare earth salts as chromate replacers for pre-treatments on galvanised steel. *Electrochim. Acta* **2004**, *49*, 2927–2935. [CrossRef]

44. Figueira, R.B. Hybrid Sol-Gel Coatings: Erosion-Corrosion Protection. *Prod. Prop. Appl. High. Temp. Coat.* **2018**, 334–380.

45. Bhandari, J.; Khan, F.; Abbassi, R.; Garaniya, V.; Ojeda, R. Modelling of pitting corrosion in marine and offshore steel structures—a technical review. *J. Loss Prev. Process. Ind.* **2015**, *37*, 39–62. [CrossRef]

46. Price, S.; Figueira, R. Corrosion Protection Systems and Fatigue Corrosion in Offshore Wind Structures: Current Status and Future Perspectives. *Coatings* **2017**, *7*, 25. [CrossRef]

47. The Global Cost and Impact of Corrosion. Available online: https://inspectioneering.com/news/2016-03-08/5202/nace-study-estimates-global-cost-of-corrosion-at-25-trillion-ann (accessed on 28 January 2020).

48. Market Research Reports, Industry Analysis, Business Overview & Trends—360 Market Updates. Available online: https://www.360marketupdates.com/aboutus (accessed on 27 January 2020).

49. Tedim, J.; Poznyak, S.K.; Kuznetsova, A.; Raps, D.; Hack, T.; Zheludkevich, M.L.; Ferreira, M.G.S. Enhancement of Active Corrosion Protection via Combination of Inhibitor-Loaded Nanocontainers. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1528–1535. [CrossRef]

50. Lakshmi, R.V.; Aruna, S.T.; Sampaith, S. Ceria nanoparticles vis-à-vis cerium nitrate as corrosion inhibitors for silica-alumina hybrid sol-gel coating. *Appl. Surf. Sci.* **2017**, *393*, 397–404.

51. Yasakau, K.A.; Ferreira, M.G.S.; Zheludkevich, M.L. Sol-Gel Coatings with Nanocontainers of Corrosion Inhibitors for Active Corrosion Protection of Metallic Materials. In *Handbook of Sol-Gel Science and Technology*; Klein, L., Aparicio, M., Jitianu, A., Eds.; Springer International Publishing: Cham, Switzerland, 2017; pp. 1–37. ISBN 978-3-319-19454-7.

52. Varma, P.C.R.; Colreavy, J.; Cassidy, J.; Oubaha, M.; McDonagh, C.; Duffy, B. Corrosion protection of AA 2024-T3 aluminium alloys using 3, 4-diaminobenzoic acid chelated zirconium–silane hybrid sol–gels. *Thin Solid Films* **2010**, *518*, 5753–5761. [CrossRef]

53. Nourani-Vatani, M.; Ganjali, M.; Solati-Hashjin, M.; Zarrintaj, P.; Reza Saeb, M. Zirconium-based hybrid coatings: A versatile strategy for biomedical engineering applications. *Mater. Today Proc.* **2018**, *5*, 15524–15531. [CrossRef]

54. Adraider, Y.; Pang, Y.X.; Nabhani, F.; Hodgson, S.N.; Sharp, M.C.; Al-Waidh, A. Fabrication of zirconium oxide coatings on stainless steel by a combined laser/sol–gel technique. *Ceram. Int.* **2013**, *39*, 9665–9670. [CrossRef]

55. Yoganandan, G.; Pradeep Premkumar, K.; Balaraju, J.N. Evaluation of corrosion resistance and self-healing behavior of zirconium–cerium conversion coating developed on AA2024 alloy. *Surf. Coat. Technol.* **2015**, *270*, 249–258. [CrossRef]

56. Catauro, M.; Bollino, F.; Papale, F.; Giovanardi, R.; Veronesi, P. Corrosion behavior and mechanical properties of bioactive sol-gel coatings on titanium implants. *Mater. Sci. Eng. C* **2014**, *43*, 375–382. [CrossRef]

57. Wen, C.E.; Xu, W.; Hu, W.Y.; Hodgson, P.D. Hydroxyapatite/titania sol-gel coatings on titanium-zirconium alloy for biomedical applications. *Acta Biomater.* **2007**, *3*, 403–410. [CrossRef]
58. Catauro, M.; Bollino, F.; Giovanardi, R.; Veronesi, P. Modification of Ti6Al4V implant surfaces by biocompatible TiO2/PCL hybrid layers prepared via sol-gel dip coating: Structural characterization, mechanical and corrosion behavior. *Mater. Sci. Eng. C* 2017, 74, 501–507. [CrossRef]

59. Thai, T.T.; Trinh, A.T.; Olivier, M.-G. Hybrid sol–gel coatings doped with cerium nanocontainers for active corrosion protection of AA2014. *Prog. Org. Coat.* 2017, 138, 105428. [CrossRef]

60. Zhang, D.; Yuan, T.; Wei, G.; Wang, H.; Gao, L.; Lin, T. Preparation of self-healing hydrophobic coating on AA6061 alloy surface and its anti-corrosion property. *J. Alloy. Compd.* 2019, 774, 495–501. [CrossRef]

61. Stankiewicz, A. 14—Self-healing nanocoatings for protection against steel corrosion. In *Nanotechnology in Eco-Efficient Construction*, 2nd ed.; Pacheco-Torgal, F., Diamanti, M.V., Nazari, A., Granqvist, C.G., Pruna, A., Amirkhanian, S., Eds.; Woodhead Publishing Series in Civil and Structural Engineering; Woodhead Publishing: Sawston, UK; Cambridge, UK, 2019; pp. 303–335. ISBN 978-0-08-102641-0.

62. Habib, S.; Khan, A.; Nawaz, M.; Sliem, M.H.; Shakoor, R.A.; Kahraman, R.; Abdullah, A.M.; Zekri, A. Self-Healing Performance of Multifunctional Polymeric Smart Coatings. *Polymers* 2019, 11, 1519. [CrossRef]

63. Yasakau, K.A.; Kuznetsova, A.; Kallip, S.; Starykevich, M.; Tedim, J.; Ferreira, M.G.S.; Zheludkevich, M.L. A novel bilayer system comprising LDH conversion layer and sol-gel coating for active corrosion protection of AA2024. *Corros. Sci.* 2018, 143, 299–313. [CrossRef]

64. Montemor, M.F.; Vicente, C. Functional Self-Healing Coatings: A New Trend in Corrosion Protection by Organic Coatings. In *Encyclopedia of Interfacial Chemistry*; Wandelt, K., Ed.; Elsevier: Oxford, UK, 2018; pp. 236–249. ISBN 978-0-12-809894-3.

65. Calado, L.M.; Taryba, M.G.; Carmezim, M.J.; Montemor, M.F. Self-healing ceria-modified coating for corrosion protection of AZ31 magnesium alloy. *Corros. Sci.* 2018, 142, 12–21. [CrossRef]

66. Adsul, S.H.; Soma Raju, K.R.C.; Sarada, B.V.; Sonawane, S.H.; Subasri, R. Evaluation of self-healing properties of inhibitor loaded nanoclay-based anticorrosive coatings on magnesium alloy AZ91D. *J. Magnes. Alloy.* 2018, 6, 299–308. [CrossRef]

67. Manasa, S.; Jyothirmayi, A.; Siva, T.; Sathiyaranayanan, S.; Gobi, K.V.; Subasri, R. Effect of inhibitor loading into nanocontainer additives of self-healing corrosion protection coatings on aluminum alloy A356.0. *J. Alloy. Compd.* 2017, 726, 969–977. [CrossRef]

68. Lutz, A.; van den Berg, O.; Wielant, J.; De Graeve, I.; Terryn, H. A Multiple-Action Self-Healing Coating. *Front. Mater.* 2016, 2, 73. [CrossRef]

69. Lutz, A.; Mol, J.M.C.; De Graeve, I.; Terryn, H. 6—Smart corrosion protection by multi-action self-healing polymeric coatings. In *Smart Composite Coatings and Membranes*; Montemor, M.F., Ed.; Woodhead Publishing Series in Composites Science and Engineering; Woodhead Publishing: Sawston, UK; Cambridge, UK, 2016; pp. 157–181. ISBN 978-1-78242-283-9.

70. Scharf, S.; Noeske, M.; Cavalcanti, W.L.; Schiffs, P. 4—Multi-functional, self-healing coatings for corrosion protection: Materials, design and processing. In *Handbook of Smart Coatings for Materials Protection*; Makhlouf, A.S.H., Ed.; Woodhead Publishing: Sawston, UK; Cambridge, UK, 2014; pp. 75–104. ISBN 978-0-85709-680-7.

71. Mittal, V. 8—Self-healing anti-corrosion coatings for applications in structural and petrochemical engineering A2—Makhlouf, Abdel Salam Hamdy. In *Handbook of Smart Coatings for Materials Protection*; Woodhead Publishing: Sawston, UK; Cambridge, UK, 2014; pp. 183–197. ISBN 978-0-85709-680-7.

72. Shchukin, D.G.; Grigoriev, D.O. 10—The use of nanoreservoirs in corrosion protection coatings. In *Corrosion Protection and Control Using Nanomaterials*; Saji, V.S., Cook, R., Eds.; Woodhead Publishing Series in Metals and Surface Engineering; Woodhead Publishing: Sawston, UK; Cambridge, UK, 2012; pp. 264–282. ISBN 978-1-84569-949-9.

73. Abdolah Zadeh, M.; van der Zwaag, S.; Garcia, S.J. Routes to extrinsic and intrinsic self-healing corrosion protective sol-gel coatings: A review. *Self-Heal. Mater.* 2013, 1, 1–18. [CrossRef]

74. Tedim, J.; Zheludkevich, M.L.; Salak, A.N.; Lisenkov, A.; Ferreira, M.G.S. Nanostructured LDH-container layer with active protection functionality. *J. Mater. Chem.)* 2011, 21, 15464–15470. [CrossRef]
76. Yasakau, K.A.; Tedim, J.; Montemor, M.F.; Salak, A.N.; Zheludkevich, M.L.; Ferreira, M.G.S. Mechanisms of Localized Corrosion Inhibition of AA2024 by Cerium Molybdate Nanowires. *J. Phys. Chem. C* 2013, 117, 5811–5823. [CrossRef]

77. Figueira, R.B.; Sousa, R.; Silva, C.J.R. Chapter 3—Multifunctional and smart organic–inorganic hybrid sol–gel coatings for corrosion protection applications. In *Advances in Smart Coatings and Thin Films for Future Industrial and Biomedical Engineering Applications*; Makhlouf, A.S.H., Abu-Thabit, N.Y., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; pp. 57–97. ISBN 978-0-12-849870-5.

78. Faustini, M.; Nicole, L.; Ruiz-Hitzky, E.; Sanchez, C. History of Organic–Inorganic Hybrid Materials: Prehistory, Art, Science, and Advanced Applications. *Adv. Funct. Mater.* 2018, 28, 1704158. [CrossRef]

79. Zub, Y.L.; Kessler, V.G. *Sol.-Gel Methods for Materials Processing: Focusing on Materials for Pollution Control, Water Purification, and Soil Remediation.*, Springer Science & Business Media: Berlin/Heidelberg, Germany, 2008; ISBN 978-1-4020-8514-7.

80. Reisfeld, R.; Jorgensen, C.K. (Eds.) *Chemistry, Spectroscopy and Applications of Sol.-Gel Glasses*; Springer: Berlin/Heidelberg, Germany, 1992; ISBN 3-540-54374-0.

81. Bergna, H.E.; Roberts, W.O. *Colloidal Silica: Fundamentals and Applications*; CRC Press: Boca Raton, FL, USA, 2005; ISBN 978-1-4200-2870-6.

82. Park, J.; Joo, J.; Kwon, S.G.; Jang, Y.; Hyeon, T. Synthesis of Monodisperse Spherical Nanocrystals. *Angew. Chem. Int. Ed.* 2007, 46, 4630–4660. [CrossRef]

83. Manez. *The Supramolecular Chemistry of Organic Inorganic Hybrid. Mater. by Manez*, Wiley: Hoboken, NJ, USA, 2010.

84. Zarzycki, J. Past and present of sol-gel science and technology. *J. Sol.-Gel Sci. Technol.* 1997, 22, 17–22. [CrossRef]

85. Gupta, R.; Chaudhury, N.K. Entrapment of biomolecules in sol–gel matrix for applications in biosensors: Problems and future prospects. *Biosens. Bioelectron.* 2007, 22, 2387–2399. [CrossRef]

86. Leite, F.R.F.; Santos, W.d.J.R.; Kubota, L.T. Selective determination of caffeic acid in wines with electrochemical sensor based on molecularly imprinted siloxanes. *Sens. Actuators B Chem.* 2014, 193, 238–246. [CrossRef]

87. Grieshaber, D.; MacKenzie, R.; Voeroes, J.; Reimhult, E. Electrochemical biosensors-Sensor principles and architectures. *Sensors* 2008, 8, 1400–1458. [CrossRef]

88. Pauliukaitė, R.; Schoenleber, M.; Vadgama, P.; Brett, C.M.A. Development of electrochemical biosensors based on sol-gel enzyme encapsulation and protective polymer membranes. *Anal. Bioanal. Chem.* 2008, 390, 1121–1131. [CrossRef] [PubMed]

89. Privett, B.J.; Shin, J.H.; Schoenfisch, M.H. Electrochemical Sensors. *Anal. Chem.* 2010, 82, 4723–4741. [CrossRef]

90. Bai, J.; Zhang, X.; Peng, Y.; Hong, X.; Liu, Y.; Jiang, S.; Ning, B.; Gao, Z. Ultrasensitive sensing of diethylstilbestrol based on AuNPs/MWCNTs-CS composites coupling with sol-gel molecularly imprinted polymer as a recognition element of an electrochemical sensor. *Sens. Actuators B Chem.* 2017, 244, 785–795. [CrossRef]

91. Choi, M.M.F. Progress in Enzyme-Based Biosensors Using Optical Transducers. *Microchim. Acta* 2004, 148, 107–132. [CrossRef]

92. Jerónimo, P.C.A.; Araújo, A.N.; Conceição, B.S.M.; Montenegro, M. Optical sensors and biosensors based on sol–gel films. *Talanta* 2007, 72, 13–27. [CrossRef] [PubMed]

93. Borisov, S.M.; Wolfsbeis, O.S. Optical Biosensors. *Chem. Rev.* 2008, 108, 423–461. [CrossRef] [PubMed]

94. Monton, M.R.N.; Forsberg, E.M.; Brennan, J.D. Tailoring Sol–Gel-Derived Silica Materials for Optical Biosensing. *Chem. Mater.* 2012, 24, 796–811. [CrossRef]

95. Wang, Y.; Tu, S.; Pinchuk, A.N.; Xiong, M.P. Active drug encapsulation and release kinetics from hydrogel-in-liposome nanoparticles. *J. Colloid Interface Sci.* 2013, 406, 247–255. [CrossRef]

96. Cho, H.; Gao, J.; Kwon, G.S. PEG-b-PLA micelles and PLGA-b-PEG-b-PLGA sol–gels for drug delivery. *J. Control. Release* 2016, 240, 191–201. [CrossRef]
98. Khamsehashari, N.; Hassanzadeh-Tabrizi, S.A.; Bigham, A. Effects of strontium adding on the drug delivery behavior of silica nanoparticles synthesized by P123-assisted sol-gel method. *Mater. Chem. Phys.* **2018**, *205*, 283–291. [CrossRef]

99. Lee, H.-Y.; Kim, H.-E.; Jeong, S.-H. One-pot synthesis of silane-modified hyaluronic acid hydrogels for effective antibacterial drug delivery via sol–gel stabilization. *Colloids Surf. B Biointerfaces* **2019**, *174*, 308–315. [CrossRef]

100. Hernández-Abad, V.J.; Sánchez-González, E.G.; Espinosa-Contreras, C.; Marroquin-Segura, R.; Mora-Guevara, J.L.A.; Flores-Cabrera, Y. Controlled release of glibenclamide from monolithic silica subdermal implants produced by the sol-gel process and its use for hyperglycaemia treatment in a murine model. *Mater. Sci. Eng. C* **2019**, *94*, 1009–1019. [CrossRef]

101. Catauro, M.; Papale, F. Coatings of titanium substrates with xCaO$_2$-ySiO$_2$ sol–gel materials: Characterization, bioactivity and biocompatibility evaluation. *Mater. Sci. Eng. C* **2016**, *58*, 846–851. [CrossRef]

102. Asri, R.I.M.; Harun, W.S.W.; Hassan, M.A.; Ghani, S.A.C.; Buyong, Z. A review of hydroxyapatite-based coating techniques: Sol–gel and electrochemical depositions on biocompatible metals. *J. Mech. Behav. Biomed. Mater.* **2016**, *57*, 95–108. [CrossRef]

103. Sidane, D.; Rammal, H.; Beljebbar, A.; Gangloff, S.C.; Chicot, D.; Velard, F.; Khireddine, H.; Montagne, A.; Kerdjoudj, H. Biocompatibility of sol-gel hydroxyapatite-titania composite and bilayer coatings. *Mater. Sci. Eng. C* **2017**, *72*, 650–658. [CrossRef] [PubMed]

104. Ramezani, S.; Rahiminejad, A.; Farzaneh, K.; Mohseni, M.; Ghanbari, H. Development of novel biocompatible hybrid nanocomposites based on polyurethane-silica prepared by sol gel process. *Mater. Sci. Eng. C* **2016**, *69*, 1248–1255. [CrossRef] [PubMed]

105. Almeida, R.M.; Fortes, L.M.; Clara Gonçalves, M. Sol–gel derived photonic bandgap coatings for solar optical applications. *Prog. Org. Coat.* **2016**, *72*, 211–218. [CrossRef]

106. Choi, Y.-E.; Kwak, J.-W.; Park, J.W. Nanotechnology for Early Cancer Detection. *Sensors* **2010**, *10*, 428–455. [CrossRef] [PubMed]

107. Mousa, S. Biosensors: The new wave in cancer diagnosis. *Nano. Technol. Sci. Appl.* **2010**, *4*, 1. [CrossRef]

108. Simon, E. Biological and chemical sensors for cancer diagnosis. *Meas. Sci. Technol.* **2010**, *21*, 112002. [CrossRef]

109. Arya, S.K.; Bhansali, S. Lung Cancer and Its Early Detection Using Biomarker-Based Biosensors. *Chem. Rev.* **2011**, *111*, 6783–6809. [CrossRef] [PubMed]

110. Baer, D.R.; Burrows, P.E.; El-Azab, A.A. Enhancing coating functionality using nanoscience and nanotechnology. *Prog. Org. Coat.* **2003**, *47*, 342–356. [CrossRef]

111. Almeida, R.M.; Fortes, L.M.; Clara Gonçalves, M. Sol–gel derived photonic bandgap coatings for solar control. *Opt. Mater.* **2011**, *33*, 1867–1871. [CrossRef]
120. Bansal, N.P.; Wise, B. Sol–gel synthesis of La$_{0.6}$Sr$_{0.4}$CoO$_{3−x}$ and Sm$_{0.5}$Sr$_{0.5}$CoO$_{3−x}$ cathode nanopowders for solid oxide fuel cells. *Ceram. Int.* 2012, 38, 5535–5541. [CrossRef]

121. Choi, Y.-G.; Park, J.-Y.; Son, J.-W.; Lee, J.-H.; Je, H.-J.; Kim, B.-K.; Lee, H.-W.; Yoon, K.J. Ceria-based electrolyte reinforced by sol–gel technique for intermediate-temperature solid oxide fuel cells. *Int. J. Hydrog. Energy* 2013, 38, 9867–9872. [CrossRef]

122. Tseng, C.-J.; Chang, J.-K.; Hung, I.-M.; Lee, K.-R.; Lee, S.-W. BaZr$_{1−x}$Ce$_x$O$_{1.5−δ}$ solid oxide fuel cell electrolyte synthesized by sol–gel combined with composition-exchange method. *Int. J. Hydrog. Energy* 2014, 39, 14434–14440. [CrossRef]

123. Chen, M.; Chu, W.; Zhu, J.; Dong, L. Plasma assisted preparation of cobalt catalysts by sol–gel method for methane combustion. *J. Sol.-Gel Sci. Technol.* 2008, 47, 354–359. [CrossRef]

124. Tichit, D.; Coq, B.; Armendariz, H. One-step sol–gel synthesis of sulfated-zirconia catalysts. *Catal. Lett.* 1996, 38, 109–113. [CrossRef]

125. Aegerter, M.A.; Mennig, M. *Sol–Gel Technologies for Glass Processors and Users*; Kluwer Academic Publishers: Boston, MA, USA, 2004; ISBN 1-4020-7938-9.

126. Dimitriev, Y.; Ivanova, Y.; Iordanova, R. History of sol-gel science and technology. *J. Univ. Chem. Technol. Metallurgy* 2008, 43, 181–192.

127. Ciriminna, R.; Fidalgo, A.; Pandarus, V.; Béland, F.; Ilharco, L.M.; Pagliaro, M. The Sol-Gel Route to Advanced Silica-Based Materials and Recent Applications. *Chem. Rev.* 2013. [CrossRef] [PubMed]

128. Gilberts, J.; Tinnemans, A.H.A.; Hogerheide, M.P.; Koster, T.P.M. UV Curable Hard Transparent Hybrid Coating Materials on Polycarbonate Prepared by the Sol-Gel Method. *J. Sol.-Gel Sci. Technol.* 1998, 11, 153–159. [CrossRef]

129. Kiruthika, P.; Subasri, R.; Jyothirmayi, A.; Sarvani, K.; Hebalkar, N.Y. Effect of plasma surface treatment on mechanical and corrosion protection properties of UV-curable sol-gel based GPTS-ZrO$_2$ coatings on mild steel. *Surf. Coat. Technol.* 2010, 204, 1270–1276. [CrossRef]

130. Senani, S.; Campazzi, E.; Villatte, M.; Druez, C. Potentiality of UV-cured hybrid sol–gel coatings for aeronautical metallic substrate protection. *Surf. Coat. Technol.* 2013, 227, 32–37. [CrossRef]

131. Detty, M.R.; Ciriminna, R.; Bright, F.V.; Pagliaro, M. Xerogel Coatings Produced by the Sol–Gel Process as ... and Recent Applications. *Chem. Rev.* 2013. [CrossRef] [PubMed]

132. Oldani, V.; Sergi, G.; Pirola, C.; Sacchi, B.; Bianchi, C.L. Sol-gel hybrid coatings containing silica and a perfluoropolyether derivative with high resistance and anti-fouling properties in liquid media. *J. Fluor. Chem.* 2018, 197, 188–197. [CrossRef]

133. Zhang, L.; Zhang, J.; Liu, R. Organic–inorganic hybrid sol–gel coatings for corrosion protection of aluminum alloys. *Surf. Innov.* 2016, 4, 51–69. [CrossRef]

134. Avcı, N.; Cimieri, I.; Smet, P.F.; Poelman, D. Stability improvement of moisture sensitive CaS:Eu$^{2+}$ micro-particles by coating with sol–gel alumina. *Opt. Mater.* 2011, 33, 1032–1035. [CrossRef]

135. Bera, S.; Rout, T.K.; Udayabhanu, G.; Narayan, R. Comparative Study of Corrosion Protection of Sol–Gel Coatings with Different Organic Functionality on Al-2024 substrate. *Prog. Org. Coat.* 2015, 88, 293–303. [CrossRef]

136. Doong, R.; Lee, P.-S.; Anitha, K. Simultaneous determination of biomarkers for Alzheimer’s disease using sol-gel-derived optical array biosensor. *Biosens. Bioelectron.* 2010, 25, 2464–2469. [CrossRef]

137. Fang, W.; Linder, M.B.; Laaksonen, P. Modification of carbon nanotubes by amphiphilic glycosylated proteins. *J. Colloid Interface Sci.* 2018, 512, 318–324. [CrossRef]

138. Kristensen, J.B.; Meyer, R.L.; Poulsen, C.H.; Kragh, K.M.; Besenbacher, F.; Laursen, B.S. Biomimetic silica encapsulation of enzymes for replacement of biocides in antifouling coatings. *Green Chem.* 2010, 12, 387–394. [CrossRef]

139. Gasiorek, J.; Szczurek, A.; Babiarczuk, B.; Kaleta, J.; Jones, W.; Krzak, J. Functionalizable Sol-Gel Silica Coatings for Corrosion Mitigation. *Materials* 2018, 11, 197. [CrossRef]

140. Doong, R.; Lee, P.-S.; Anitha, K. Simultaneous determination of biomarkers for Alzheimer’s disease using sol-gel-derived optical array biosensor. *Biosens. Bioelectron.* 2010, 25, 2464–2469. [CrossRef]
142. Choi, J.-W.; Kang, D.-Y.; Jang, Y.-H.; Kim, H.-H.; Min, J.; Oh, B.-K. Ultra-sensitive surface plasmon resonance based immunosensor for prostate-specific antigen using gold nanoparticle–antibody complex. *Colloids Surf. A Physicochem. Eng. Asp.* 2008, 313–314, 655–659. [CrossRef]

143. DeLisa, M.P.; Zhang, Z.; Shiloach, M.; Pilevar, S.; Davis, C.C.; Sirkis, J.S.; Bentley, W.E. Evanscense wave long-period fiber bragg grating as an immobilized antibody biosensor. *Anal. Chem.* 2000, 72, 2895–2900. [CrossRef]

144. Mujahid, A.; Dickert, F.L. Chemical Sensors Based on Molecularly Imprinted Sol-Gel Materials. *Materials* 2010, 3, 2196–2217. [CrossRef]

145. Shrivastava, S.; Jadon, N.; Jain, R. Next-generation polymer nanocomposite-based electrochemical sensors and biosensors: A review. *TrAC Trends Anal. Chem.* 2016, 82, 55–67. [CrossRef]

146. Suginta, W.; Khunkaewla, P.; Schulte, A. Electrochemical Biosensor Applications of Polysaccharides Chitin and Chitosan. *Chem. Rev.* 2013, 113, 5458–5479. [CrossRef] [PubMed]

147. Matsuhisa, H.; Tsuchiya, M.; Hasebe, Y. Protein and polysaccharide-composite sol–gel silicate film for an interference-free amperometric glucose biosensor. *Colloids Surf. B Biointerfaces* 2013, 111, 523–529. [CrossRef] [PubMed]

148. Dahl, J.A.; Maddux, B.L.S.; Hutchison, J.E. Toward greener nanosynthesis. *Chem. Rev.* 2007, 107, 2228–2269. [CrossRef] [PubMed]

149. Zheludkevich, M.L.; Tedim, J.; Ferreira, M.G.S. “Smart” coatings for active corrosion protection based on multi-functional micro and nancontainers. *Electrochim. Acta* 2012, 82, 314–323. [CrossRef]

150. Carneiro, J.; Tedim, J.; Fernandes, S.C.M.; Freire, C.S.R.; Gandini, A.; Ferreira, M.G.S.; Zheludkevich, M.L. Chitosan as a Smart Coating for Controlled Release of Corrosion Inhibitor 2-Mercaptobenzothiazole. *ECS Electrochem. Lett.* 2013, 2, C19–C22. [CrossRef]

151. Abu-Thabit, N.Y.; Hamdy, A.S. Stimuli-responsive Polyelectrolyte Multilayers for fabrication of self-healing coatings—a review. *Surf. Coat. Technol.* 2016, 303, 406–424. [CrossRef]

152. Alaneme, K.K.; Bodunrin, M.O. Self-healing using metallic material systems—a review. *Appl. Mater. Today* 2017, 6, 9–15. [CrossRef]

153. Samiee, R.; Ramezanzadeh, B.; Mahdavian, M.; Alibakhshi, E. Assessment of the smart self-healing corrosion protection properties of a water-base hybrid organo-silane film combined with non-toxic organic/inorganic environmentally friendly corrosion inhibitors on mild steel. *J. Clean. Prod.* 2019, 220, 340–356. ISBN 978-3-527-67081-9.

154. Innocenzi, P.; Malfatti, L. Processing of Sol–Gel Films from a Top-Down Route. In *The Sol-Gel Handbook*; Levy, D., Zayat, R., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2015; pp. 165–194. ISBN 978-3-527-67081-9.

155. Durán, A.; Castro, Y.; Conde, A.; de Damborenea, J.J. Sol–Gel Protective Coatings for Metals. In *Handbook of Sol-Gel Science and Technology*; Klein, L., Aparicio, M., Jitianu, A., Eds.; Springer International Publishing: Cham, Switzerland, 2016; pp. 1–65. ISBN 978-3-319-19454-7.

156. Wang, D.; Bierwagen, G.P. Sol–gel coatings on metals for corrosion protection. *Prog. Org. Coat.* 2009, 64, 327–338. [CrossRef]

157. Cushing, B.L.; Kolesnichenko, V.L.; O’Connor, C.J. Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles. *Chem. Rev.* 2004, 104, 3893–3946. [CrossRef]

158. Yamasaki, S.; Sakuma, W.; Yasui, H.; Daicho, K.; Saito, T.; Fujisawa, S.; Isogai, A.; Kanamori, K. Frontiers Nanocellulose Xerogels With High Porosities and Large Specific Surface Areas Chemistry. Available online: https://www.frontiersin.org/articles/10.3389/fchem.2019.00316/full (accessed on 4 March 2020).

159. Polyurethane/Ionic Silica Xerogel Composites for CO2 Capture. Available online: http://www.scielo.br/scielo.php?script=sci_arttext&pid=S1516-14392019000700228 (accessed on 4 March 2020).

160. Pierre, A.C.; Pajonk, G.M. Chemistry of Aerogels and Their Applications. *Chem. Rev.* 2002, 102, 4243–4266. [CrossRef] [PubMed]

161. Boev, V.I.; Soloviev, A.; Silva, C.J.R.; Gomes, M.J.M.; Barber, D.J. Highly transparent sol-gel derived ureasilicate monoliths exhibiting long-term optical stability. *J. Sol.-Gel Sci. Technol.* 2006, 41, 223–229. [CrossRef]
163. Zhang, G.; Dass, A.; Rawashdeh, A.-M.M.; Thomas, J.; Counsil, J.A.; Sotiriou-Leventis, C.; Fabrizio, E.F.; Ilhan, F.; Vassilaras, P.; Scheiman, D.A.; et al. Isocyanate-crosslinked silica aerogel monoliths: Preparation and characterization. *J. Non-Cryst. Solids* **2004**, *350*, 152–164.

164. Moreira, S.D.F.C.; Silva, C.J.R.; Prado, L.A.S.A.; Costa, M.F.M.; Boev, V.I.; Martin-Sánchez, J.; Gomes, M.J.M. Development of new high transparent hybrid organic-inorganic monoliths with surface engraved diffraction pattern. *J. Polym. Sci. Part. B Polym. Phys.* **2012**, *50*, 492–499. [CrossRef]

165. Xu, J.; Liu, Y.; Du, W.; Lei, W.; Si, X.; Zhou, T.; Lin, J.; Peng, L. Superhydrophobic silica antireflective coatings with high transmittance via one-step sol-gel process. *Thin Solid Films* **2017**, *631*, 193–199. [CrossRef]

166. Esposito, S. “Traditional” Sol-Gel Chemistry as a Powerful Tool for the Preparation of Supported Metal and Metal Oxide Catalysts. *Materials* **2019**, *12*, 668. [CrossRef] [PubMed]

167. Bescher, E.; Hoshino, Y.; Nishizawa, Y.; Cooley, K.; Mackenzie, J.D. The Role of Fe in the Thermal Stabilization of Ormosils. *J. Sol.-Gel Sci. Technol.* **2003**, *26*, 297–301. [CrossRef]

168. Shilova, O. Synthesis and structure features of composite silicate and hybrid TEOS-derived thin films doped by inorganic and organic additives. *J. Sol.-Gel Sci. Technol.* **2013**, *68*, 387–410. [CrossRef]

169. Argente-García, A.; Muñoz-Ortuño, M.; Molins-Legua, C.; Moliner-Martínez, Y.; Campiñas-Falcó, P. A solid device based on doped hybrid composites for controlling the dosage of the biocide N-(3-aminopropyl)-N-dodecyl-1,3-propanediamine in industrial formulations. *Talanta* **2016**, *147*, 147–154. [CrossRef]

170. Subbiah, K.; Han-Seung, L.; Yun Su, L.; Jitendra Kumar, S.; Seung-Jun, K.; Rethinam, N. Fabrication of a cerium-doped nickel ferrite solid-state reference electrode and its performance evaluation in concrete environment. *Sens. Actuators B Chem.* **2017**, *251*, 509–523. [CrossRef]

171. Wojcik, A.; Klein, L.C. Transparent organic/inorganic hybrid gels: A classification scheme. *Appl. Organomet. Chem.* **1997**, *11*, 129–135. [CrossRef]

172. Xing, W.; You, B.; Wu, L. Chemical and anticorrosion characterization of polysilsesquioxane coatings catalyzed by different acids. *J. Coat. Technol. Res.* **2008**, *5*, 65–72. [CrossRef]

173. Loy, D.A.; Obrey-DeFriend, K.A.; Wilson, K.V.; Minke, M.; Baugher, C.R.; Schneider, D.A.; Jamison, G.M.; Shea, K.J. Influence of the alkoxide group, solvent, catalyst, and concentration on the gelation technique in the modern coating industry. *RSC Adv.* **2016**, *6*, 106964–106979. [CrossRef]
184. Guo, X.; Zhang, Q.; Ding, X.; Shen, Q.; Wu, C.; Zhang, L.; Yang, H. Synthesis and application of several sol–gel-derived materials via sol–gel process combining with other technologies: A review. J. Sol.-Gel Sci. Technol. 2016, 79, 328–358. [CrossRef]
185. Zvonkina, I.; Soucek, M. Inorganic–organic hybrid coatings: Common and new approaches. Curr. Opin. Chem. Eng. 2016, 11, 123–127. [CrossRef]
186. Ulaeto, S.B.; Rajan, R.; Pancrecius, J.K.; Rajan, T.P.D.; Pai, B.C. Developments in smart anticorrosive coatings with multifunctional characteristics. Prog. Org. Coat. 2017, 111, 294–314. [CrossRef]
187. Eduok, U.; Faye, O.; Szpunar, J. Recent developments and applications of protective silicone coatings: A review of PDMS functional materials. Prog. Org. Coat. 2017, 111, 124–163. [CrossRef]
188. Fihri, A.; Bovero, E.; Al-Shahrani, A.; Al-Ghamdi, A.; Alabedi, G. Recent progress in superhydrophobic coatings used for steel protection: A review. Colloids Surf. A Physicochem. Eng. Asp. 2017, 520, 378–390. [CrossRef]
189. Aparicio, M.; Mosa, J. Electrochemical characterization of sol–gel coatings for corrosion protection of metal substrates. J. Sol.-Gel. Sci. Technol. 2018, 88, 77–89. [CrossRef]
190. Barroso, G.; Li, Q.; Bordia, R.K.; Motz, G. Polymeric and ceramic silicon-based coatings—a review. J. Mater. Chem. A 2019, 7, 1936–1963. [CrossRef]
191. Chou, T.; Chandrasekaran, C.; Cao, G.Z. Sol-gel-derived hybrid coatings for corrosion protection. J. Sol.-Gel Sci. Technol. 2003, 26, 321–327. [CrossRef]
192. Hammer, P.; Santos, F.C.; dos Cerrutti, B.M.; Pulcinelli, S.H.; Santilli, C.V. Highly corrosion resistant siloxane-polyethylmethacrylate hybrid coatings. J. Sol.-Gel Sci. Technol. 2012, 63, 266–274. [CrossRef]
193. Balan, P.; Ng, A.; Beng Siang, C.; Singh Raman, R.K.; Chan, E.S. Effect of Nanoparticle Addition in Hybrid Sol-Gel Silane Coating on Corrosion Resistance of Low Carbon Steel. Adv. Mater. Res. 2013, 686, 244–249. [CrossRef]
194. Fedel, M.; Callone, E.; Diré, S.; Deflorian, F.; Olivier, M.-G.; Poelman, M. Effect of Na-Montmorillonite sonication on the protective properties of hybrid silica coatings. Electrochim. Acta 2014, 124, 92–99. [CrossRef]
195. Habazaki, H.; Kimura, T.; Aoki, Y.; Tsuji, E.; Yano, T. Highly Enhanced Corrosion Resistance of Stainless Steel by Sol-Gel Layer-by-Layer Alumino-silicate Thin Coatings. J. Electrochem. Soc. 2013, 161, C57–C61. [CrossRef]
196. Hernandez, M.; Barba, A.; Genesca, J.; Covelo, A.; Bucio, E.; Torres, V. Characterization of Hybrid Sol-Gel Coatings Doped with Hydrotalcite-like Compounds on Steel and Stainless Steel Alloys. ECS Trans. 2013, 47, 195–206. [CrossRef]
197. Claire, L.; Marie, G.; Julien, G.; Jean-Michel, S.; Jean, R.; Marie-Jolle, M.; Stefano, R.; Michele, F. New architectured hybrid sol-gel coatings for wear and corrosion protection of low-carbon steel. Prog. Org. Coat. 2016, 99, 337–345. [CrossRef]
198. Maia, F.; Yasakau, K.A.; Carneiro, J.; Kallip, S.; Tedim, J.; Henriques, T.; Cabral, A.; Venâncio, J.; Zheludkevich, M.L.; Ferreira, M.G.S. Corrosion protection of AA2024 by sol–gel coatings modified with MBT-loaded polyurea microcapsules. Chem. Eng. J. 2016, 283, 1108–1117. [CrossRef]
199. Sarmento, V.H.V.; Schiavetto, M.G.; Hammer, P.; Benedetti, a.V.; Fugivara, C.S.; Suegama, P.H.; Pulcinelli, S.H.; Santilli, C.V. Corrosion protection of stainless steel by polysiloxane hybrid coatings prepared using the sol–gel process. Surf. Coat. Technol. 2010, 204, 2689–2701. [CrossRef]
200. Cambron, J.-B.; Ansart, F.; Bonino, J.-P.; Turq, V. Effect of cerium concentration on corrosion resistance and polymerization of hybrid sol–gel coating on martensitic stainless steel. Prog. Org. Coat. 2012, 75, 486–493. [CrossRef]
205. Tan, A.L.K.; Soutar, A.M. Hybrid sol–gel coatings for corrosion protection of copper. *Thin Solid Film.* 2008, 516, 5706–5709. [CrossRef]

206. Li, Y.-S.; Lu, W.; Wang, Y.; Tran, T. Studies of (3-mercaptopropyl)trimethoxysilane and bis(trimethoxysilyl)ethane sol–gel coating on copper and aluminum. *Spectrochim. Acta. Part. A Mol. Biomol. Spectrosc.* 2009, 73, 922–928. [CrossRef]

207. Karthik, N.; Lee, Y.R.; Sethuraman, M.G. Hybrid sol–gel/thiourea binary coating for the mitigation of copper corrosion in neutral medium. *Prog. Org. Coat.* 2017, 102, 259–267. [CrossRef]

208. Khramov, A.N.; Bablyshev, V.N.; Kasten, L.S.; Mantz, R.A. Sol–gel coatings with phosphonate functionalities for surface modification of magnesium alloys. *Thin Solid Films* 2006, 514, 174–181. [CrossRef]

209. Montemor, M.F.; Ferreira, M.G.S. Electrochemical study of modified bis-(triethoxysilylpropyl) tetrasulfide silane films applied on the AZ31 Mg alloy. *Electrochim. Acta* 2007, 52, 7486–7495. [CrossRef]

210. Lamaka, S.V.; Montemor, M.F.; Galio, A.F.; Zheludkevich, M.L.; Trindade, C.; Dick, L.F.; Ferreira, M.G.S. Inhibitor-doped sol–gel coatings for corrosion protection of AZ31B magnesium alloy. *Electrochim. Acta* 2008, 53, 4773–4783. [CrossRef]

211. Khramov, A.N.; Johnson, J.A. Phosphonate-functionalized ORMOSIL coatings for magnesium alloys. *Prog. Org. Coat.* 2009, 65, 381–385. [CrossRef]

212. Galio, A.F.; Lamaka, S.V.; Zheludkevich, M.L.; Dick, L.F.P.; Müller, I.L.; Ferreira, M.G.S. Inhibitor-doped sol–gel coatings for corrosion protection of magnesium alloy AZ31. *Surf. Coat. Technol.* 2010, 204, 1479–1486. [CrossRef]

213. Adsul, S.H.; Siva, T.; Sathiyanarayanan, S.; Sonawane, S.H.; Subasri, R. Self-healing ability of nanoclay-based hybrid sol–gel coatings on magnesium alloy AZ91D. *Surf. Coat. Technol.* 2017, 309, 609–620. [CrossRef]

214. Nezamdoust, S.; Seifzadeh, D.; Rajabalizadeh, Z. PTMS/OM–MWCNT sol–gel nanocomposite for corrosion protection of magnesium alloy. *Surf. Coat. Technol.* 2018, 335, 228–240. [CrossRef]

215. Roudi, P.; Milošev, I. Corrosion Inhibition of Pure Aluminium and Alloys AA2024-T3 and AA7075-T6 by Cerium(III) and Cerium(IV) Salts. *J. Electrochem. Soc.* 2016, 163, C85–C93. [CrossRef]

216. Shchukin, D.G.; Lamaka, S.V.; Montemor, M.F. Smart composite coatings for corrosion protection of aluminium alloys in aerospace applications. In *Smart Composite Coatings and Membranes;* Elsevier: Amsterdam, The Netherlands, 2016; pp. 85–121. ISBN 978-1-78242-283-9.

217. Vignesh, R.B.; Balaji, J.; Sethuraman, M.G. Surface modification, characterization and corrosion protection of 1,3-diphenylthiourea doped sol–gel coating on aluminium. *Prog. Org. Coat.* 2017, 111, 112–123. [CrossRef]

218. Khandanjou, S.; Ghoranneviss, M.; Saviz, S. The detailed analysis of the spray time effects of the aluminium coating using self-generated atmospheric plasma spray system on the microstructure and corrosion behaviour. *Results Phys.* 2017, 7, 1440–1445. [CrossRef]

219. Roudi, P.; Milošev, I.; Lekka, M.; Andreattta, F.; Fedrizzi, L. Corrosion behaviour and chemical stability of transparent hybrid sol–gel coatings deposited on aluminium in acidic and alkaline solutions. *Prog. Org. Coat.* 2018, 124, 286–295. [CrossRef]

220. Tiringer, U.; Milošev, I.; Durán, A.; Castro, Y. Hybrid sol–gel coatings based on GPTMS/TEOS containing colloidal SiO2 and cerium nitrate for increasing corrosion protection of aluminium alloy 7075-T6. *J. Sol.-Gel Sci. Technol.* 2018, 945, 546–557. [CrossRef]

221. Shchukin, D.G.; Möhwald, H. Surface-Engineered Nanocontainers for Entrapment of Corrosion Inhibitors. *Adv. Funct. Mater.* 2007, 17, 1451–1458. [CrossRef]

222. Balaskas, A.C.; Kartsonakis, I.A.; Tziveleka, L.A.; Kordas, G.C. Improvement of anti-corrosive properties of epoxy-coated AA 2024-T3 with TiO2 nanocontainers loaded with 8-hydroxyquinoline. *Prog. Org. Coat.* 2012, 74, 418–426. [CrossRef]

223. Borisova, D.; Möhwald, H.; Shchukin, D.G. Influence of embedded nanocontainers on the efficiency of active anticorrosive coatings for aluminium alloys part II: Influence of nanocontainer position. *ACS Appl. Mater. Interfaces* 2013, 5, 80–87. [CrossRef] [PubMed]

224. Alibakhshi, E.; Ghasemi, E.; Mahdavian, M.; Ramezanzadeh, B. A comparative study on corrosion inhibitive effect of nitrate and phosphate intercalated Zn-Al- layered double hydroxides (LDHs) nanocontainers incorporated into a hybrid silane layer and their effect on cathodic delamination of epoxy topcoat. *Corros. Sci.* 2017, 115, 159–174. [CrossRef]
225. Caldarelli, A.; Raimondo, M.; Veronesi, F.; Boveri, G.; Guarini, G. Sol–gel route for the building up of superhydrophobic nanostructured hybrid-coatings on copper surfaces. Surf. Coat. Technol. 2015, 276, 408–415. [CrossRef]

226. Wei, H.; Wang, Y.; Guo, J.; Shen, N.Z.; Jiang, D.; Zhang, X.; Yan, X.; Zhu, J.; Wang, Q.; Shao, L.; et al. Advanced micro/nanocapsules for self-healing smart anticorrosion coatings. J. Mater. Chem. A 2014, 3, 469–480. [CrossRef]

227. Thakur, V.K.; Kessler, M.R. Self-healing polymer nanocomposite materials: A review. Polymer 2015, 69, 369–383. [CrossRef]

228. Zahidah, K.A.; Kakooei, S.; Ismail, M.C.; Bothi Raja, P. Halloysite nanotubes as nanocontainer for smart protective coatings: A review. Corros. Sci. 2018, 144, 74–88. [CrossRef]

229. Wei, H.; Wang, Y.; Guo, J.; Shen, N.Z.; Jiang, D.; Zhang, X.; Yan, X.; Zhu, J.; Wang, Q.; Shao, L.; et al. Advanced micro/nanocapsules for self-healing smart anticorrosion coatings. J. Mater. Chem. A 2014, 3, 469–480. [CrossRef]

227. Thakur, V.K.; Kessler, M.R. Self-healing polymer nanocomposite materials: A review. Polymer 2015, 69, 369–383. [CrossRef]
246. Dry, C.M.; Sottos, N.R. Passive smart self-repair in polymer matrix composite materials. In Proceedings of the Smart Structures and Materials 1993: Smart Materials, International Society for Optics and Photonics, Albuquerque, NM, USA, 23 July 1993; pp. 438–445.

247. White, S.R.; Sottos, N.R.; Geubelle, P.H.; Moore, J.S.; Kessler, M.R.; Sriram, S.R.; Brown, E.N.; Viswanathan, S. Autonomic healing of polymer composites. *Nature* 2001, 409, 794–797. [CrossRef]

248. White, S.R.; Sottos, N.R.; Geubelle, P.H.; Moore, J.S.; Kessler, M.R.; Sriram, S.R.; Brown, E.N.; Viswanathan, S. Autonomic healing of polymer composites. *Nature* 2001, 409, 794–797. [CrossRef]

249. Cho, S.H.; White, S.R.; Braun, P.V. Self-Healing Polymer Coatings. *Adv. Mater.* 2009, 21, 645–649. [CrossRef]

250. Garcí́a, S.J.; Fischer, H.R.; White, P.A.; Mardel, J.; Gonzalez-García, Y.; Mol, J.M.C.; Hughes, A.E. Self-healing anticorrosive organic coating based on an encapsulated water reactive silyl ester: Synthesis and proof of concept. *Prog. Org. Coat.* 2011, 70, 142–149. [CrossRef]

251. Snihirova, D.; Lamaka, S.V.; Taryba, M.; Salak, A.N.; Kallip, S.; Zheludkevich, M.L.; Ferreira, M.G.S.; Montemor, M.F. Hydroxyapatite Microparticles as Feedback-Active Reservoirs of Corrosion Inhibitors. *ACS Appl. Mater. Interfaces* 2010, 2, 3011–3022. [CrossRef]

252. Carneiro, J.; Tedim, J.; Fernandes, S.C.M.; Freire, C.S.R.; Silvestre, A.J.D.; Gandini, A.; Ferreira, M.G.S.; Zheludkevich, M.L. Chitosan-based self-healing protective coatings doped with cerium nitrate for corrosion protection of aluminum alloy 2024. *Prog. Org. Coat.* 2012, 75, 8–13. [CrossRef]

253. Zheludkevich, M.L.; Shchukin, D.G.; Yasakau, K.A.; Möhwald, H.; Ferreira, M.G.S. Anticorrosion Coatings with Self-Healing Effect Based on Nanocontainers Impregnated with Corrosion Inhibitor. *Chem. Mater.* 2007, 19, 402–411. [CrossRef]

254. Zheludkevich, M.L.; Poznyak, S.K.; Rodrigues, L.M.; Raps, D.; Hack, T.; Dick, L.F.; Nunes, T.; Ferreira, M.G.S. Active protection coatings with layered double hydroxide nanocontainers of corrosion inhibitor. *Corrosion Sci.* 2010, 52, 602–611. [CrossRef]

255. Zheludkevich, M.L.; Tedim, J.; Freire, C.S.R.; Fernandes, S.C.M.; Kallip, S.; Lisenkov, A.; Gandini, A.; Ferreira, M.G.S. Self-healing protective coatings with “green” chitosan based pre-layer reservoir of corrosion inhibitor. *J. Mater. Chem.* 2011, 21, 4805–4812. [CrossRef]

256. Yasakau, K.A.; Zheludkevich, M.L.; Karavai, O.V.; Ferreira, M.G.S. Influence of inhibitor addition on the corrosion protection performance of sol–gel coatings on AA2024. *Prog. Org. Coat.* 2008, 63, 352–361. [CrossRef]

257. Maia, F.; Tedim, J.; Lisenkov, A.D.; Salak, A.N.; Zheludkevich, M.L.; Ferreira, M.G.S. Silica nanocontainers for active corrosion protection. *Nanoscale* 2012, 4, 1287–1298. [CrossRef]

258. Montemor, M.F.; Snihirova, D.V.; Taryba, M.G.; Lamaka, S.V.; Kartsonakis, I.A.; Balaskas, A.C.; Kordas, G.C.; Tedim, J.; Kuznetsova, A.; Zheludkevich, M.L.; et al. TEM and EDS analysis of self-healing ability in protective coatings modified with combinations of layered double hydroxides and cerium molibdate nanocontainers filled with corrosion inhibitors. *Electrochim. Acta* 2012, 60, 31–40. [CrossRef]

259. Audsul, S.H.; Siva, T.; Sathiyanarayanan, S.; Sonawane, S.H.; Subasri, R. Aluminum pillared montmorillonite clay-based self-healing coatings for corrosion protection of magnesium alloy AZ91D. *Surf. Coat. Technol.* 2018, 352, 445–461. [CrossRef]

260. Kim, B.-M.; Saravanan, M.; Lee, D.-H.; Kang, J.-H.; Kim, M.; Jung, J.-H.; Rhee, J.-S. Exposure to sublethal concentrations of tributyltin reduced survival, growth, and 20-hydroxyecdysone levels in a marine mysid. *Mar. Environ. Res.* 2018, 140, 96–106. [CrossRef]

261. Barletta, M.; Aversa, C.; Pizzi, E.; Puopolo, M.; Vesco, S. Design, development and first validation of “biocide-free” anti-fouling coatings. *Prog. Org. Coat.* 2018, 123, 35–46. [CrossRef]

262. Detty, M.R.; Ciriminna, R.; Bright, F.V.; Pagliaro, M. Environmentally benign sol-gel antifouling and foul-releasing coatings. *Acc. Chem. Res.* 2014, 47, 678–687. [CrossRef]

263. Wouters, M.; Rentrop, C.; Willemansen, P. Surface structuring and coating performance: Novel biocidefree nanocomposite coatings with anti-fouling and fouling-release properties. *Prog. Org. Coat.* 2010, 68, 4–11. [CrossRef]

264. Wallström, E.; Jespersen, H.T.; Schaumburg, K. A new concept for anti-fouling paint for Yachts. *Prog. Org. Coat.* 2011, 72, 109–114. [CrossRef]
265. Zheng, Z.; Huang, X.; Schenderlein, M.; Borisova, D.; Cao, R.; Möhwald, H.; Shchukin, D. Self-Healing and Anti-fouling Multifunctional Coatings Based on pH and Sulfide Ion Sensitive Nanocontainers. Adv. Funct. Mater. 2013, 23, 3307–3314. [CrossRef]

266. Akuzov, D.; Vladkova, T.; Zamfirova, G.; Gaydarov, V.; Nascimento, M.V.; Szeglat, N.; Grunwald, I. Polydime-thyl siloxane coatings with superior antibiofouling efficiency in laboratory and marine conditions. Prog. Org. Coat. 2017, 103, 126–134. [CrossRef]

267. Trentin, I.; Romainne, V.; Marcenaro, G.; De Carolis, G. Quick test methods for marine anti-fouling paints. Prog. Org. Coat. 2001, 42, 15–19. [CrossRef]

268. Almeida, E.; Diamantino, T.C.; de Sousa, O. Marine paints: The particular case of anti-fouling paints. Prog. Org. Coat. 2007, 59, 2–20. [CrossRef]

269. Faÿ, F.; Linossier, I.; Peron, J.J.; Langlois, V.; Vallée-Rehel, K. Antifouling activity of marine paints: Study of erosion. Prog. Org. Coat. 2007, 60, 194–206. [CrossRef]

270. Faÿ, F.; Linossier, I.; Legendre, G.; Vallée-Rehel, K. Micro-Encapsulation and Anti-fouling Coatings: Development of Poly(lactic acid) Microspheres Containing Bioactive Molecules. Macromol. Symp. 2008, 272, 45–51. [CrossRef]

271. Lejars, M.; Margaillan, A.; Bressy, C. Fouling Release Coatings: A Nontoxic Alternative to Biocidal Anti-fouling Coatings. Chem. Rev. 2012, 112, 4347–4390. [CrossRef]

272. Carpeau, D.; Vallée-Rehel, K.; Linossier, I.; Quiniou, F.; Davy, R.; Compère, C.; Delbur, M.; Faÿ, F. Development of environmentally friendly anti-fouling paints using biodegradable polymer and lower toxic substances. Prog. Org. Coat. 2014, 77, 485–493. [CrossRef]

273. Telegdi, J.; Trif, L.; Románszki, L. 5—Smart anti-biofouling composite coatings for naval applications A2—Montemor, M.F. In Smart Composite Coatings and Membranes; Woodhead Publishing Series in Composites Science and Engineering; Woodhead Publishing: Sawston, UK; Cambridge, UK, 2016; pp. 123–155. ISBN 978-1-78242-283-9.

274. Palanchamy, S.; Subramanian, G. Anti-fouling properties of marine bacteriocin incorporated epoxy based paint. Prog. Org. Coat. 2017, 103, 33–39. [CrossRef]

275. Oldani, V.; del Negro, R.; Bianchi, C.L.; Suriano, R.; Turri, S.; Pirola, C.; Sacchi, B. Surface properties and anti-fouling assessment of coatings obtained from perfluoropolyethers and ceramic oxides nanopowders deposited on stainless steel. J. Fluor. Chem. 2015, 180, 7–14. [CrossRef]

276. Junaidi, M.U.M.; Ahmad, N.N.R.; Leo, C.P.; Yee, H.M. Near superhydrophobic coating synthesized from rice

277. Movahedi, A.; Zhang, J.; Kann, N.; Moth-Poulsen, K.; Nyd, M. Copper-coordinating polymers for marine antifouling coatings: A physicochemical and electrochemical study of ternary system of copper, PMMA and poly(TBTA). Prog. Org. Coat. 2016, 97, 216–221. [CrossRef]

278. Yang, W.; Zhao, W.; Liu, Y.; Hu, H.; Pei, X.; Wu, Y.; Zhou, F. The effect of wetting property on anti-fouling/foul-release performance under quasi-static/hydrodynamic conditions. Prog. Org. Coat. 2016, 95, 64–71. [CrossRef]

279. Barletta, M.; Aversa, C.; Pizzi, E.; Puopolo, M.; Vesco, S. Design, manufacturing and testing of anti-fouling/foul-release (AF/FR) amphiphilic coatings. Prog. Org. Coat. 2013, 123, 267–281. [CrossRef]

280. Li, Y.; Ning, C. Latest research progress of marine microbiological corrosion and bio-fouling, and new approaches of marine anti-corrosion and anti-fouling. Bioact. Mater. 2019, 4, 189–195. [CrossRef]

281. Olsen, S.M.; Kristensen, J.B.; Laursen, B.S.; Pedersen, L.T.; Dam-Johansen, K.; Kiil, S. Anti-fouling effect of hydrogen peroxide release from enzymatic marine coatings: Exposure testing under equatorial and Mediterranean conditions. Prog. Org. Coat. 2010, 68, 248–257. [CrossRef]

282. Zanaroli, G.; Negroni, A.; Calisti, C.; Ruzzi, M.; Fava, F. Selection of commercial hydrolytic enzymes with potential anti-fouling activity in marine environments. Enzym. Microb. Technol. 2011, 49, 574–579. [CrossRef]

283. Meißler, M.; Taden, A.; Börner, H.G. Enzyme-Triggered Anti-fouling Coatings: Switching Bioconjugate Adsorption via Proteolytically Cleavable Interfering Domains. ACS Macro Lett. 2016, 5, 583–587. [CrossRef]

284. Krupa, A.N.D.; Vimala, R. Evaluation of tetraethoxysilane (TEOS) sol–gel coatings, modified with green synthesized zinc oxide nanoparticles for combating microfouling. Mater. Sci. Eng. C 2016, 61, 728–735. [CrossRef] [PubMed]
285. Holberg, S.; Losada, R.; Blaikie, F.H.; Hansen, H.H.W.B.; Sorea, S.; Onderwater, R.C.A. Hydrophilic silicone coatings as fouling release: Simple synthesis, comparison to commercial, marine coatings and application on fresh water-cooled heat exchangers. Mater. Today Commun. 2020, 22, 100750. [CrossRef]

286. Arukalam, I.O.; Oguzie, E.E.; Li, Y. Fabrication of FDTS-modified PDMS-ZnO nanocomposite hydrophobic coating with anti-fouling capability for corrosion protection of Q235 steel. J. Colloid Interface Sci. 2016, 484, 220–228. [CrossRef] [PubMed]

287. Nuraini, L.; Prifiharni, S.; Priyotomo, G.; Sundjono, Gunawan, H. Evaluation of anticorrosion and anti fouling paint performance after exposure under seawater Surabaya–Madura (Suramadu) bridge. Aip Conf. Proc. 2017, 1823, 020101.

288. Superhydrophobic Surfaces. Available online: https://www.crcpress.com/Superhydrophobic-Surfaces/Carre-Mittal/p/book/9789004165939 (accessed on 4 March 2019).

289. Nishimoto, S.; Bhushan, B. Bioinspired self-cleaning surfaces with superhydrophobicity, superoleophobicity, and superhydrophilicity. RSC Adv. 2012, 3, 671–690. [CrossRef]

290. Montazer, M.; Harifi, T. 12—Water-repellent textile nanofinishes. In Nanofinishing of Textile Materials; Montazer, M., Harifi, T., Eds.; The Textile Institute Book Series; Woodhead Publishing: Sawston, UK; Cambridge, UK, 2018; pp. 183–195. ISBN 978-0-08-101214-7.

291. Varanasi, K.K.; Deng, T.; Hsu, M.F.; Bhate, N. Corrosion behavior of superhydrophobic surfaces: American Society of Mechanical Engineers: New York, NY, USA, 2008; pp. 637–645.

292. Zhang, D.; Wang, L.; Qian, H.; Li, X. Superhydrophobic surfaces for corrosion protection: A review of recent progresses and future directions. J. Coat. Technol. Res. 2015, 13, 11–29. [CrossRef]

293. Barkhudarov, P.M.; Shah, F.B.; Watkins, E.B.; Doshi, D.A.; Brinker, C.J.; Majewski, J. Corrosion inhibition using superhydrophobic films. Corros. Sci. 2008, 50, 897–902. [CrossRef]

294. Maeztu, J.D.; Rivero, P.J.; Berlanga, C.; Bastidas, D.M.; Palacio, J.F.; Rodriguez, R. Effect of graphene oxide and fluorinated polymeric chains incorporated in a multilayered sol-gel nanocoating for the design of corrosion resistant and hydrophobic surfaces. Appl. Surf. Sci. 2017, 419, 138–149. [CrossRef]

295. Calabrese, L.; Bonaccorsi, L.; Capri, A.; Proverbio, E. Adhesion aspects of hydrophobic silane zeolite coatings for corrosion protection of aluminum substrate. Prog. Org. Coat. 2014, 77, 1341–1350. [CrossRef]

296. Bescher, E.P.; Noori, A.; Mackenzie, J.D. Fluorinated Copolymer-Oxide Hybrids. J. Sol.-Gel Sci. Technol. 2004, 32, 69–72. [CrossRef]

297. Mohamed, A.M.A.; Abdullah, A.M.; Younan, N.A. Corrosion behavior of superhydrophobic surfaces: A review. Arab. J. Chem. 2015, 8, 749–765. [CrossRef]

298. Matin, A.; Merah, N.; Ibrahim, A. Superhydrophobic and self-cleaning surfaces prepared from a commercial silane using a single-step drop-coating method. Prog. Org. Coat. 2016, 99, 322–329. [CrossRef]

299. Vasiljević, J.; Tomšić, B.; Jerman, I.; Orel, B.; Jakša, G.; Kovač, J.; Simončič, B. Multifunctional superhydrophobic/oleophobic and flame-retardant cellulose fibres with improved ice-releasing properties and passive antibacterial activity prepared via the sol–gel method. J. Sol.-Gel Sci. Technol. 2014, 70, 385–399.

300. Latthe, S.S.; Sudhagar, P.; Devadoss, A.; Kumar, A.M.; Liu, S.; Terashima, C.; Nakata, K.; Fujishima, A. A mechanically bendable superhydrophobic steel surface with self-cleaning and corrosion-resistant properties. J. Mater. Chem. A 2015, 3, 14263–14271. [CrossRef]

301. Zhang, L.; Zuo, W.; Li, T. Controlled synthesis of bifunctional PbWO4 dendrites via a facile solution method at room temperature: Photoluminescence and superhydrophobic property. Mater. Sci. Semicond. Process. 2015, 39, 188–191. [CrossRef]

302. Zhang, J.; Xu, Z.; Mai, W.; Min, C.; Zhou, B.; Shan, M.; Li, Y.; Yang, C.; Wang, Z.; Qian, X. Improved hydrophilicity, permeability, anti fouling and mechanical performance of PVDF composite ultrafiltration membranes tailored by oxidized low-dimensional carbon nanomaterials. J. Mater. Chem. A 2013, 1, 3101–3111. [CrossRef]

303. Jurgis Philipavičius, I.K. Hydrophobic Antireflective Silica Coatings via Sol-gel Process. Medziagotrya 2008, 14, 283–287.

304. Lakshmi, R.V.; Bharathidasan, T.; Basu, B.J. Superhydrophobic sol–gel nanocomposite coatings with enhanced hardness. Appl. Surf. Sci. 2011, 257, 10421–10426. [CrossRef]

305. Meera, K.M.S.; Sankar, R.M.; Murail, A.; Jaisankar, S.N.; Mandal, A.B. Sol-gel network silica/modified montmorillonite clay hybrid nanocomposites for hydrophobic surface coatings. Colloids Surf. B Biointerfaces 2012, 90, 204–210. [CrossRef]
306. Cai, S.; Zhang, Y.; Zhang, H.; Yan, H.; Lv, H.; Jiang, B. Sol-gel preparation of hydrophobic silica antireflective coatings with low refractive index by base/acid two-step catalysis. ACS Appl. Mater. Interfaces 2014, 6, 11470–11475. [CrossRef]
307. Oldani, V.; Sergi, G.; Pirola, C.; Bianchi, C.L. Use of a sol-gel hybrid coating composed by a fluoropolymer and silica for the mitigation of mineral fouling in heat exchangers. Appl. Therm. Eng. 2016, 106, 427–431. [CrossRef]
308. Sharma, V.; Sharma, V.; Goyat, M.S.; Hooda, A.; Pandey, J.K.; Kumar, A.; Gupta, R.; Upadhyay, A.K.; Prakash, R.; Kirabira, J.B.; et al. Recent progress in nano-oxides and CNTs based corrosion resistant superhydrophobic coatings: A critical review. Prog. Org. Coat. 2020, 140, 105512. [CrossRef]
309. Huang, X.; Tepylo, N.; Pommier-Budinger, V.; Budinger, M.; Bonaccurso, E.; Villedieu, P.; Bennani, L. A survey of icerophobic coatings and their potential use in a hybrid coating/active ice protection system for aerospace applications. Prog. Aerosp. Sci. 2019, 105, 74–97. [CrossRef]
310. Xu, L.; He, J. Fabrication of Highly Transparent Superhydrophobic Coatings from Hollow Silica Nanoparticles. Langmuir 2012, 28, 7512–7518. [CrossRef]
311. Wankhede, R.G.; Morey, S.; Khanna, A.S.; Birbills, N. Development of water-repellent organic–inorganic hybrid sol–gel coatings on aluminium using short chain perfluoro polymer emulsion. Appl. Surf. Sci. 2013, 283, 1051–1059. [CrossRef]
312. Shang, Q.; Wang, M.; Liu, H.; Gao, L.; Xiao, G. Facile fabrication of water repellent coatings from vinyl functionalized SiO2 spheres. J. Coat. Technol. Res. 2013, 10, 465–473. [CrossRef]
313. Mokhtari, S.; Karimzadeh, F.; Abbasi, M.H.; Raeissi, K. Development of stable and Mechanically Robust Superhydrophobic Surfaces Made from Porous Silica Capsules. Adv. Mater. 2010, 22, 230–235. [CrossRef]
314. Lee, J.-W.; Hwang, W. Exploiting the silicon content of aluminum alloys to create a superhydrophobic surface using the sol–gel process. Mater. Lett. 2016, 168, 83–85. [CrossRef]
315. Liang, J.; Hu, Y.; Wu, Y.; Chen, H. Facile formation of superhydrophobic silica-based surface on aluminum substrate with tetraethyloxysilicate and vinyltriethoxysilane as co-precursor and its corrosion resistant performance in corrosive NaCl aqueous solution. Surf. Coat. Technol. 2014, 240, 145–153. [CrossRef]
316. Li, X.; Zhang, Q.; Guo, Z.; Shi, T.; Yu, J.; Tang, M.; Huang, X. Fabrication of superhydrophobic surface with improved corrosion inhibition on 6061 aluminum alloy substrate. Appl. Surf. Sci. 2015, 342, 76–83. [CrossRef]
317. Zheng, S.; Li, C.; Fu, Q.; Hu, W.; Xiang, T.; Wang, Q.; Du, M.; Liu, X.; Chen, Z. Development of stable superhydrophobic coatings on aluminum surface for corrosion-resistant, self-cleaning, and anti-icing applications. Mater. Des. 2016, 93, 261–270. [CrossRef]
318. Foroo shani, H.M.; Aliofkhazraei, M.; Rouhaghdam, A.S. Superhydrophobic aluminum surfaces by mechanical/chemical combined method and its corrosion behavior. J. Taiwan Inst. Chem. Eng. 2017, 72, 220–235. [CrossRef]
319. Rao, A.V.; Latthe, S.S.; Mahadik, S.A.; Kappenstein, C. Mechanically stable and corrosion resistant superhydrophobic sol–gel coatings on copper substrate. Appl. Surf. Sci. 2011, 257, 5772–5776. [CrossRef]
320. Wang, S.; Guo, X.; Xie, Y.; Liu, L.; Yang, H.; Zhu, R.; Gong, J.; Peng, L.; Ding, W. Preparation of superhydrophobic silica film on Mg–Nd–Zn–Zr magnesium alloy with enhanced corrosion resistance by combining micro-arc oxidation and sol–gel method. Surf. Coat. Technol. 2012, 213, 192–201. [CrossRef]
321. Wu, L.-K.; Zhang, X.-F.; Hu, J.-M. Corrosion protection of mild steel by one-step electrodeposition of superhydrophobic silica film. Corros. Sci. 2014, 85, 482–487. [CrossRef]
322. Zhang, X.-F.; Chen, R.-J.; Hu, J.-M. Superhydrophobic surface constructed on electrodeposited silica films by two-step method for corrosion protection of mild steel. Corros. Sci. 2016, 104, 336–343. [CrossRef]
323. Valipour Motlagh, N.; Birjandi, F.C.; Sargolzaei, J.; Shahtahmassebi, N. Durable, superhydrophobic, superoleophobic and corrosion resistant coating on the stainless steel surface using a scalable method. Appl. Surf. Sci. 2013, 283, 636–647. [CrossRef]
324. Wang, Q.; Li, J.; Zhang, C.; Qu, X.; Liu, J.; Yang, Z. Regenerative superhydrophobic coating from microcapsules. J. Mater. Chem. 2010, 20, 3211–3215. [CrossRef]
325. Deng, X.; Mammen, L.; Zhao, Y.; Lellig, P.; Mülken, K.; Li, C.; Butt, H.-J.; Vollmer, D. Transparent, Thermally Stable and Mechanically Robust Superhydrophobic Surfaces Made from Porous Silica Capsules. Adv. Mater. 2011, 23, 2962–2965. [CrossRef]
326. Zhao, X.; Li, Y.; Li, B.; Hu, T.; Yang, Y.; Li, L.; Zhang, J. Environmentally benign and durable superhydrophobic coatings based on SiO2 nanoparticles and silanes. J. Colloid Interface Sci. 2019, 542, 8–14. [CrossRef]
327. Milionis, A.; Loth, E.; Bayer, I.S. Recent advances in the mechanical durability of superhydrophobic materials. Adv. Colloid Interface Sci. 2016, 229, 57–79. [CrossRef] [PubMed]
328. Ellinas, K.; Tserepi, A.; Gogolides, E. Durable superhydrophobic and superamphiphobic polymeric surfaces and their applications: A review. Adv. Colloid Interface Sci. 2017, 250, 132–157. [CrossRef] [PubMed]

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