Remediation of Fouling on Painted Steel Roofing via Solar Energy Assisted Photocatalytic Self-Cleaning Technology: Recent Developments and Future Perspectives

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Rainwater harvesting on roofs is a sustainable solution for global water scarcity. The contamination of roofing materials due to biological organisms and other environmental pollutants limits the utilization of roof harvested rainwater for domestic and industrial applications. Similarly, roof contamination leads to several aesthetic, functional, and environmental concerns highlighting the importance of developing green self-cleaning technology for roofing applications. Solar-energy-driven semiconductor-based photocatalytic self-cleaning coatings are a promising approach to minimizing roof contamination against both biological and non-biological pollutants. However, the development of such technology on painted steel substrates for long-term outdoor applications has become limited due to the number of challenges are analyzed in this review. Accordingly, challenges, recent developments, and future perspectives of developing and evaluating the performance of photocatalytic self-cleaning coating systems for roofing applications have been critically reviewed in this article analyzing the research findings of recent studies.

1. Introduction

The depletion of freshwater resources is a global crisis in fulfilling domestic and industrial water demand. Rainwater harvesting is a sustainable solution for minimizing the global impact of water scarcity. Therefore, the studies related to the collection of potable rainwater from roof runoff have become a significant research area with high demand. However, the roof contamination due to biological organisms and other environmental pollutants has challenged the usage of roof run-off rainwater as an alternative water resource for domestic and industrial applications due to health and environmental concerns. For example, according to a recent random study, only 18% of roof-collected rainwater samples have been compiled with the water quality standards of New Zealand.

According to another study, about 50% of roof harvested rainwater has been contaminated with E. coli leading to health concerns. Therefore roof contamination has become a significant challenge in establishing roof water harvesting technologies for domestic and industrial applications.

The water quality levels of roof-harvested rainwater systems at different geological locations have been assessed in recent studies as summarized in Table 1. A significant concentration of contaminants has been detected including microorganisms, organic pollutants, inorganic pollutants, and metal substances, highlighting the challenge of utilizing for domestic and industrial requirements. Accordingly, the level of contaminants needs to be removed before recommending as an alternative water source. Self-cleaning coatings are a promising approach to minimizing roof contamination. Specifically, solar-assisted photocatalytic self-cleaning coating technology is ideal due to its extended activity toward a broad spectrum of pollutants.

The roof contaminants are classified into biological and non-biological pollutants based on the source of the origin. The biological contamination occurs due to the colonization of microbial species on roofing substrates. The non-biological contaminants such as dust, particles of combustion products, organic pollutants, fallen tree leaves/debris, wood-based materials, acidic gases (SO$_2$, NO$_2$), salts, and ozone also lower the quality of roof harvested rainwater and accelerate roof deterioration. The majority of contaminants are adsorbed to the roof surface from external sources. However, a certain percentage of contaminants can also be leached out from the internal roof coatings and roofing materials due to deterioration. Climatic parameters such as sunlight, rain, and humidity are also...
negatively influential on roof deterioration resulting in an increase of leach out of the roofing materials with rainwater over time.\[9\] As an example, the prolonged exposure of painted roofing materials to a high level of solar radiation leads to photo-degradation and thermal degradation, resulting in weakening of the chemical properties and leach out issues.\[9\] The retention of rainwater and moisture under fallen tree leaves and debris accelerate microbial growth, further enhancing biological contamination and associated problems.

Roof-collected rainwater is contaminated mainly via three stages as shown in Figure 1. Atmospheric pollutants are contaminated with rainwater before contacting the roof surface as shown in Figure 1 under the “air wash out” category. Importantly the atmospheric pollutant levels of adjacent layers are also purified in presence of a self-cleaning roofing system. Furthermore the contamination due to “roof wash out” is also minimized on self-cleaning roofs due to its self-oxidizing power of surface-bound pollutants in presence of solar energy. The rainwater storage tanks can also be modified with self-cleaning coating technologies to improve the quality of the water harvest. Accordingly, all three phenomena of rainwater contamination can be controlled by using the self-cleaning coating technologies expecting a significant improvement of the quality of roof-harvested rainwater for domestic and industrial applications.

Even though self-cleaning coatings seem to be the ideal solution to remediate fouling and improve the quality of roof-harvested rainwater, such applications have not yet been commercialized due to multiple challenges. The challenges and strategies to overcome those challenges have been discussed comprehensively in the later of this article in Section 6.

The biological contamination due to colonization of microbial species is a significant challenge on roofing materials. It limits the applications of roof-collected rainwater harvesting for domestic and industrial applications. Furthermore, the roof coatings are damaged due to the activities of microbial colonization on roofing materials increasing water permeability and porosity of the coating layers.\[10\] As a result, the gloss, color, and mechanical properties are deteriorated over time, weakening the physico-chemical stability of the roofing system.\[11\] Microbial-induced corrosion has also been reported as another critical effect on steel roofing.\[12\] Accordingly, roof discoloration, loss of gloss, and appearance of colored stains have been identified as early signs of microbial colonization on a painted roofing substrate highlighting the risks of biological contamination.\[13\]

### Table 1. Quality of roof-harvested rainwater systems in different urban sites.\[167\]

| –          | ON, Canada | South Korea | France | South Africa |
|------------|------------|-------------|--------|--------------|
| pH         | Median     | Range       | Median | Range        |
|            | 7.5        | 7.0-8.1     | 7.3    | 6.7-7.8      |
|            | 6.2        | 5.6-10.4    | 5.3    | 4.5-6.5      |
| Conductivity [μs cm⁻¹] | n.m.\(^a\) | n.m.\(^a\) | 30     | 6-82         |
|            | 6.8        | 2.9-9.8     | 2.4    | 0.54-7.8     |
|            | 0.09       | 0.06-0.39   | 0.32   | <0.1-1.7     |
| Nitrate [mg L⁻¹]  | n.m.\(^a\) | n.m.\(^a\) | 0.02   | 0-0.04       |
|            | <0.1-0.54  | n.d.\(^b\) | n.d.\(^b\) |
| NH₄ [mg L⁻¹]     | n.m.\(^a\) | n.m.\(^a\) | 7.5    | 5-18         |
|            | 1.7        | 0.55-4.0    | 21.2   | 16.7-29.9    |
| Chloride [mg L⁻¹] | n.m.\(^a\) | n.m.\(^a\) | 6.4    | 3.2-15.4     |
|            | 1.0-19.0   | 11.6        | 10.5-14.2 |
| Magnesium [mg L⁻¹] | low\(^c\) | low\(^c\) | 1.2    | 0.5-2.7      |
|            | 0.24       | <0.1-0.7    | 1.6    | 1.3-2.1      |
| Sodium [mg L⁻¹]  | low\(^c\)  | low\(^c\)  | 3.2    | 2.2-6.1      |
|            | 0.93       | 0.3-2.9     | 15.4   | 11.8-22.3    |
| Potassium [mg L⁻¹] | n.m.\(^a\) | n.m.\(^a\) | 3.1    | 1.3-5.9      |
|            | 0.78       | 0.15-4.9    | 2.7    | 1.7-6.3      |
| Sulfates [mg L⁻¹] | n.m.\(^a\) | n.m.\(^a\) | 4.1    | 2-7.2        |
|            | 1.8        | 0.50-6.6    | 7.9    | 3.7-19.5     |
| Mn [μg L⁻¹]     | <50        | 0-50        | 115    | 70-170       |
|            | 0.4        | 0.1-1.8     | 11.6   | 10.5-14.2    |
| Pb [μg L⁻¹]     | <10        | 0-10        | 27     | 10-40        |
|            | 0.2        | 0.1-0.4     | 11.6   | 10.5-14.2    |
| Cu [μg L⁻¹]     | <10⁴       | 0-10³       | 85     | 70-120       |
|            | 1.9        | 0.7-3.7     | 11.6   | 10.5-14.2    |
| Cr [μg L⁻¹]     | n.m.\(^a\) | n.m.\(^a\) | 4.5    | 0-10         |
|            | 0.8        | 0.5-1.7     | 11.6   | 10.5-14.2    |
| Cd [μg L⁻¹]     | <5         | 0-5         | 1.5    | 0-4          |
|            | 0.1        | 0.06-0.6    | 11.6   | 10.5-14.2    |
| As [μg L⁻¹]     | <1         | 0-1         | 3      | 0-6          |
|            | 0.5        | 0.3-0.8     | 11.6   | 10.5-14.2    |
| Zn [μg L⁻¹]     | <500       | 100-500     | 160    | 120-280      |
|            | 3.9        | 0.6-15.8    | 11.6   | 10.5-14.2    |
| Al [μg L⁻¹]     | <100       | 0-100       | 225    | 100-400      |
|            | 78.3       | 37.8-130.2  | 11.6   | 10.5-14.2    |
| Total coliforms [CFU-100 mL⁻¹] | <1 | 0-398  | 70   | 0-320        |
|            | 40         | <10⁻¹⁰⁻⁴    | 50     | 0-105        |
| E. coli [CFU-100 mL⁻¹] | n.m.\(^a\) | n.m.\(^a\) | 10    | 0-60         |
|            | 2         | <10⁻⁵⁻⁵⁰⁰  | 50     | 0-104        |
| Enterococci | n.m.\(^a\) | n.m.\(^a\) | n.m.\(^a\) | 45       | <10⁻¹⁰⁻⁸⁹⁰ |
|            | <30        | <30⁻³⁻⁴⁻⁵⁻⁹ | 9.5   | <4.0-9.5     |

\(^a\)n.m. = not measured. \(^b\)n.d. = not detected. \(^c\)Low = detected in very low concentrations (not specified).
Furthermore, the stains are generated due to the formation of microbial colonies, fungal spores, molds, and mildew on a roof resulting in visual damage. The color and shape of the stain are determined by the type and density of surface present microorganisms.\(^1\) As an example, *Gloeocapsa magma*, a type of cyanobacteria, is commonly identified on roofs as dark spots or black streaks.\(^1\) The accumulation of dead colonies of cyanobacteria has been identified as dark stains on light-colored roofing.\(^9\) However, the detailed mechanisms of microbiological deterioration on metallic roofing materials are still poorly understood. The bio-mineralization processes have taken place via the electrochemical reactions in the presence of the extracellular enzymes at the biofilm–metal interface.\(^1\)

Iden#fi#cation of the most critical and dominant microorganisms on pre-painted steel is vital in developing a self-cleaning technology. Cladosporium species, Bacillus species, Cyanobacteria, Actinobacteria, Epicoccum nigrum, and Teratosphaeriaceae species have been identified as the most dominant organisms on painted steel roofing according to the findings of a recent study.\(^1\) Furthermore, fungi have been identified as the most critical roof contaminant class that present on pre-painted steel.\(^1\) Cyanobacteria and algae have been identified as the most dominant microbial type that colonized on roofing located in humid areas of the USA, Latin America, and Europe.\(^6,8,16\) Furthermore, fungi and cyanobacteria can survive even under harsh environmental conditions such as extreme temperature conditions, discontinuous nutrient loading, high UV exposure, and repetitive cycles of desiccation and rehydration by forming stable biofilms and spores strengthening the adaptation further to stress conditions.\(^20,21\)

The contamination of roofing materials due to non-biological atmospheric pollutants is another crucial factor leading to various aesthetic, functional, and environmental concerns.\(^2\) As an example, the rate of roof deterioration is increased in proportion to the atmospheric pollutant levels shortening the service life.\(^2\) The average life cycles of the roofs that are located in marine, geothermal, and industrial zones having a higher density of atmospheric pollutant levels are relatively shorter than the villages and rural areas with a less density of atmospheric pollutants.\(^2\) Organic pollutants such as volatile organic compounds (VOC), halogenated hydrocarbons, and polynaromatic hydrocarbons (PAH) are also made a significant impact on the deterioration of building materials and the quality of roof-harvested rainwater as reported in recent publications.\(^25,26\)

Accordingly, the minimization of both biological and non-biological contamination on a roof is an important global requirement to maintain aesthetic, functional, and environmental requirements throughout the expected service life. Similarly, the minimization of roof contamination and accumulation is important to maintain the required water quality standards of roof harvested rainwater as an alternative source for global water scarcity. Solar-assisted semiconductor photocatalysis is known to be a promising technology for establishing self-cleaning coatings.
for roofing applications. Such coatings have the potential of destroying both biological and non-biological contaminants as has been discussed in Section 3 of this review. The mechanisms of photocatalytic self-cleaning activity of a roof coating system have been discussed in Section 2 to understand the modes of action.

Furthermore, roof contamination has become a substantial challenge in the global construction sector due to various aesthetic, functional, and environmental concerns not limiting to the challenges of rainwater harvesting. Staining, discoloration, dust deposition, microbial colonization, growth of fungi, algae, and lichens are some common consequences of roof contamination, as shown in Figure 2. The flow of rainwater over a contaminated roof leads to environmental pollution due to the mixing of roof contaminants with groundwater and reservoirs. However, the conventional roof cleaning processes are also challenging due to high cost, accessing limitations, the toxicity of cleaning chemicals, labor, and time requirements. Therefore, the development of sustainable self-cleaning technology for roofing applications is important to minimize the problems associated with roof contamination and fouling.

2. Self-Cleaning Mechanisms and Modes of Action

The ability to clean its surface without an additional effort and the minimization of surface contamination within the system without any external influence is referred to as self-cleaning technology.[27] Photocatalysis and surface hydrophilicity are important factors in determining the self-cleaning activity of a surface.

2.1. Photocatalysis

Photocatalysts are used to accelerate the rate of specific chemical reactions upon the absorption of photons from light.[28] The spontaneous oxidation of surface contaminants on photocatalytic materials in the presence of sunlight/UV radiation, water, and oxygen is one such useful reaction that can be used for self-cleaning applications. Titanium dioxide (TiO₂) is the most widely used semiconductor photocatalyst in commercial applications.[29]

A specific amount of photons (hγ) are absorbed by the electrons of TiO₂ molecules in the presence of UV and solar radiation, resulting in excitation of its outermost electrons according to the Planck’s equation: E = hγ where E—energy, γ—frequency, and h—Planck’s constant (h = 6.626 × 10⁻³⁴ Js).[30] Predominantly, the electrons in the 2p orbital of oxygen (valance band of TiO₂) are excited and transited into the 3d orbital (conduction band of TiO₂) resulting in an electron (e⁻)–hole (h⁺) pair. A significant fraction of these electrons (e⁻) and holes (h⁺) can be recombined due to the Coulombic interactions on oppositely charged particles. The remaining fractions of these excited particles [(e⁻) and (h⁺)] are diffused onto the surface of the bulk TiO₂ particles and undergo redox reactions at the surface. Hydroxyl radicals (OH⁻) and superoxide radicals (O₂⁻) are generated from the reaction of these surface presence excited particles [(e⁻) and (h⁺)] in the presence of water (H₂O) and oxygen (O₂). The detailed mechanism of the formation of these radicals (OH⁻ and O₂⁻) can be explained in the following reactions.[31]

The generation of photoexcited electron–hole pair [(e⁻) and (h⁺)] on the surface of TiO₂ is shown in the following chemical reaction.

![Figure 2. Consequences of roof contamination.](image-url)
Hydroxyl radicals are produced by the reaction of surface presence excited holes \((h^+_{VB})\) with water that has been adsorbed onto the TiO\(_2\) surface, as shown in the following reaction.

\[
\text{TiO}_2(h^+_{VB}) + \text{H}_2\text{O}(\text{ads}) \rightarrow \text{TiO}_2 + \text{H}^+ + \text{OH}^-
\]  

Similarly, the hydroxyl \((\text{OH}^-)\) radicals are also be formed due to the reaction of surface presence excited holes \((h^+_{VB})\) with hydroxide ions, as shown below.

\[
\text{TiO}_2(h^+_{VB}) + \text{OH}^-_{\text{ads}} \rightarrow \text{TiO}_2 + \text{OH}^-
\]  

The photoexcited electrons \((e^-_{CB})\) are reacted with oxygen forming superoxide radicals \((\text{O}_2^-)\), as shown in the following reaction.

\[
\text{TiO}_2(e^-_{CB}) + \text{O}_2_{\text{ads}} \rightarrow \text{TiO}_2 + \text{O}_2^-
\]  

These superoxide radicals are reacted with protons to generate hydroperoxyl radicals, as shown in the below reaction.

\[
\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^-
\]  

Hydrogen peroxide and oxygen are produced due to the disproportionation of these hydroperoxyl radicals.

\[
2\text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\]  

These hydrogen peroxides are reduced back into hydroxyl radicals by gaining the excited electrons \((e^-_{CB})\) from TiO\(_2\) particles, as shown in the following reaction.

\[
\text{H}_2\text{O}_2 + \text{TiO}_2(e^-_{CB}) \rightarrow \text{OH}^- + \text{OH}^-
\]  

The electron potential energy and half-life values of the \(\text{OH}^-, \text{HO}_2^-,\) and \(\text{O}_2^-\) radicals are used to confirm the higher oxidizing power and reactivity of these reactive oxygen species (ROS) as summarized in Table 2. Accordingly, \(\text{OH}^-\) can be identified as the most promising and effective ROS type for photo-initiated self-cleaning reactions due to its higher electron potential value and relatively shorter half-life value. The contaminants are photo-oxidized easily due to the high reactivity of \(\text{OH}^-, \text{HO}_2^-,\) and \(\text{O}_2^-\) radicals that are generated due to the excitation of photocatalytic coatings in presence of solar energy.

The photodegradation products are completely removed during the self-cleaning process. Complete oxidation occurs in organic pollutants resulting in gaseous carbon dioxide and water as shown in Figure 3. Similar mechanisms are involved in oxidizing inorganic pollutants resulting by-products of its highest oxidation number. Accordingly, a complete removal is expected from all oxidizable roof pollutants confirming that they are safe enough for domestic and industrial applications. However, a certain percentage of non-oxidizable pollutants and intermediate products can still be present in roof-harvested rainwater and that needs to be purified further before releasing for domestic water requirement.

| Radical    | Electron potential \([E^\circ]^{[172]}\) | Half-life \([t_{1/2}]^{[17]}\) |
|------------|---------------------------------|-------------------------|
| \(\text{OH}^-\) | +2.31 V for \(\text{OH}^-/\text{H}_2\text{O}\) | \(10^{-5}\) s |
| \(\text{HO}_2^-\) | +1.06 V for \(\text{HO}_2^-/\text{H}_2\text{O}_2\) | \(1-30\) s |
| \(\text{O}_2^-\) | −0.35 V for \(\text{O}_2/\text{O}_2^-\) + 0.91 V for \(\text{O}_2^-/\text{H}_2\text{O}_2\) | \(10^{-6}\) s |

Table 2. Electron potential and half-life values of reactive oxygen species.\(^{[171,172]}\)

Figure 3. Photo-oxidation mechanism of pollutants in presence of the solar energy. Reproduced with permission.\(^{[18]}\) 2022, Elsevier.
A large number of contaminants have been identified on roofs and in roof-harvested water as discussed in the introduction section. The chemistry of each class of roof contaminants is different and extended to a wide range. Accordingly, the photo-oxidation mechanisms of different roof contaminants have become unique and need to be addressed separately. However, radical initiated chemical bond cleavages (beta-scission), isomerization of intermediate products, polymerization, and cross-linking of photogenerated products can be identified as some common reaction modes that occurred in photocatalytic coating systems. As an example, the photodegradation of acrylic and ether structures is shown in Figure 4.

2.2. Superhydrophilicity and Superhydrophobicity

The concept of self-cleaning technology has been inspired by nature and can be explained using the lotus effect as a role model. The lotus effect of lotus leaves is based on its surface superhydrophobicity. The contaminants on a lotus leaf are picked up by water droplets and washed away by rolling off due to the low surface energy (high surface tension) created by the micro- and nanoscopic architecture on the lotus leaf surface. Rice leaves, butterfly wings, peacock feathers, water strider legs, and insect compound eyes are some other natural examples of self-cleaning substrates. The existence of rods-like texture in the size of 3–10 μm with 70–100 nm-sized valleys tinted with a waxy material has been identified on the surface of the lotus leaves in microscopic studies as shown in Figure 5. A copper hydroxide nanosized needle array has been identified as the self-cleaning structural arrangement in water striders. A considerable number of studies have been conducted on creating superhydrophobic self-cleaning surfaces using polydimethylsiloxane (PDMS), waxes, fluoropolymers, and laser fabrication for different applications such as textiles, flooring, kitchen appliances, bathroom applications, automobile mirrors, and construction materials.

Superhydrophilicity and superhydrophobicity are two extreme effects of surface wettability. Both of these phenomena are currently used in different self-cleaning applications. The strong intermolecular interactions of superhydrophilic surfaces with water facilitate the formation of a thin water film on the superhydrophilic surface by complete spreading. Therefore the contaminants that are sitting on a superhydrophilic surface are efficiently washed away, bypassing the water underneath the contaminants, as shown in Figure 6. In contrast, the water droplets are repelled and rolled off on the superhydrophobic surfaces while picking up the loosely bound surface contaminants, as described in the previous paragraph. Therefore both superhydrophobic and superhydrophilic surfaces are used in self-cleaning applications for decontamination.

The hydrophilicity of a surface is quantified using the magnitude of the water contact angle (θ) based on the Young–Dupré equation by considering the surface wettability. The contact

Figure 4. Photooxidation mechanism of a) acrylic and b) ether. Reproduced with permission. 2022, Elsevier.
angle is defined as the angle, measured through the liquid, where the liquid–air interface meets the coating surface when a tangent line is drawn from the contact point of the coating, liquid, and air[38] as shown in Figure 7. An equilibrium contact angle is obtained when a liquid drop is placed on a surface at constant temperature and pressure. The relationship between the interfacial energies per unit area at different phases of the system at the thermodynamic equilibrium is given by Young’s relation, as shown in the following equation. Where is, sl and lv are defined as the interfacial energy per unit area of the solid–vapor, solid–liquid, and liquid–vapor interfaces respectively, and θ is defined as the contact angle.[39]

\[
\gamma_{sv} = \gamma_{sl} - \gamma_{lv}\cos\theta
\]  

(8)

The surfaces can be categorized into four classes as shown in Figure 8, depending on the magnitude of the contact angle (θ) as: 1) superhydrophilic (if θ < 5°) where the liquid is evenly spread on the surface as a thin film, 2) hydrophilic (5° < θ < 90°), 3) hydrophobic (90° < θ < 150°), and 4) superhydrophobic (150° < θ < 180°) where the liquid is repelled from the surface and rolled off.[40]

2.3. Photoinduced Hydrophilicity

The spontaneous transformation of surface hydrophilicity from the original hydrophobic state to a superhydrophilic state in the presence of photons is known as photo-induced hydrophilicity (PIH),[41] as shown in Figure 9. The PIH effect is a characteristic feature of some photocatalytic materials such as TiO₂ and ZnO.[42] As an example, the hydrophobic TiO₂ surface is converted to a superhydrophilic state over time in the presence of UV radiation.[43,44] The attraction of nonpolar contaminants onto these photocatalytic coatings becomes minimal due to the lack of intermolecular interactions after achieving the PIH state. Furthermore, the contaminants can easily be washed off in the presence of rainwater by passing underneath the contaminants forming a thin film on the TiO₂ photocatalytic coating surfaces due to the firm, attractive forces between water and superhydrophilic surface.[36] However, the PIH is a reversible process, and hence can be reverted to its original hydrophobic state over time in the absence of UV radiation.[16]

The mechanisms of the PIH effect have been studied in detail in some of the recent publications.[36,44,45] Generation of surface vacancies, photoinduced reconstruction of Ti–OH bonds, and
photocatalytic decomposition of organic adsorbents have been identified as the main steps involved in the formation of the PIH effect. Oxygen vacancies are formed on the TiO$_2$ surface due to the diffusion of photogenerated holes onto the surface. As a result, the Ti$^{4+}$ sites are reduced into Ti$^{3+}$, resulting in the dissociation of water molecules via adsorption of –OH groups onto the surface of TiO$_2$.

According to the findings of a recent study, the reconstruction of Ti–OH bonds during the PIH effect is shown in Figure 10. Furthermore, the Ti–OH bonds can be lengthened and weakened due to the activity of the diffused photogenerated holes. The adsorption of water molecules can rupture the Ti–OH bond and facilitate the formation of new OH groups on the TiO$_2$ surface by eliminating a proton. In the end, one hydroxyl group which is previously bi-coordinated to a Ti atom at two sites is converted into two separate OH groups which are coordinated at a single site as shown in Figure 10.

According to the findings of a recent study, the superhydrophilic state is achieved after photo-oxidation of surface presence oxidizable contaminants. However, a combined mechanism has been suggested in the recent literature explaining the...
occurrence of both photocatalytic oxidations and PIH as a parallel process as shown in Figure 11.\textsuperscript{[45]} Initially, the surface presence oxidizable contaminants are decomposed due to the activity of photogenerated hydroxyl (OH\textsuperscript{−}) and peroxy (OOH\textsuperscript{−}) radicals in the presence of UV radiation. Only a slight reduction has been observed in contact angle measurements during this initial photo-oxidation period. However, a rapid decrease of contact angle has been observed after a critical point of photo-oxidation of surface presence contaminants. In this second step, a higher number of photo-generated holes are involved in formation of oxygen vacancies at the TiO\textsubscript{2} surface enhancing the adsorption of water.

3. Feasibility Studies

A significant number of studies have been confirmed the photo-oxidation power of TiO\textsubscript{2} against critical roof contaminants. Some of such findings are summarized in Table 3. Reactive oxygen species (ROS), which are generated in the presence of UV irradiation of TiO\textsubscript{2} photocatalysts, are involved in the photo-oxidizing reactions of roof contaminants as explained mechanisms in Section 2.1. ROS can easily attack the weakest chemical sites and bonds in the contaminant’s chemical structure, resulting in complete photo-oxidation over a series of chemical reactions.\textsuperscript{[49]} Accordingly, organic contaminants are photo-oxidized completely into gaseous CO\textsubscript{2} and H\textsubscript{2}O, resulting in none of the solid or liquid residues on the coating surface after complete photo-oxidation.\textsuperscript{[50,51]}

The detailed photo-oxidation mechanism varies depending on the chemical structure of the contaminant. Accordingly, different killing mechanisms have been proposed in recent literature describing the influence of ROS on biological pollutants. As an example, the killing mechanism of bacteria has been described as the damage of membrane and cell wall due to ROS.\textsuperscript{[52,53]} These results have been generated using analytical techniques such as microscopic detection of lipid peroxidation products and spectroscopic studies. In another study, the disruption of the cell membrane of Bacillus licheniformis due to the activity of photogenerated ROS has been identified as shown in the scanning electron microscopy (SEM) images in Figure 12.\textsuperscript{[52]} Another study has confirmed the antimicrobial activity as inhibition of deoxyribonucleic
Table 3. Literature evidence to prove the potential of photocatalysts for self-cleaning applications.

| Photocatalyst | Tested Organism/ Pollutant | References |
|---------------|----------------------------|------------|
| TiO₂          | Bacteria                   | [173]      |
|               | Bacterial and fungal spores|            |
|               | Model biofilm components   |            |
| TiO₂          | Gram-negative bacteria     | [174]      |
|               | Gram-positive bacteria     |            |
|               | Filamentous fungi          |            |
|               | Unicellular fungi          |            |
|               | Algae                      |            |
|               | Protozoa                   |            |
|               | Mammalian viruses          |            |
|               | Bacteriophage              |            |
|               | Bacterial endospores       |            |
|               | Fungal spores              | (Active against more than 200 species) |
| TiO₂ and ZnO  | Cladosporium sp. (fungi)   | [175]      |
| TiO₂          | Karenia brevis (alage)     | [176]      |
|               | Skeletonema costatum (algae)| [180] |
| TiO₂          | Algae                      | [177]      |
|               | Rotifers (platyzoa)        |            |
| P₂₅ TiO₂ and WO₂ | Oedogonium (algae)   | [178]      |
| P₂₅ TiO₂ co-catalyst: Pd | Anabaenoflos-aquae (cyanobacteria) | [179] |
|               | Methylene blue as the model pollutant | |
| TiO₂          | Scenedesmus quadricauda (algae)| [180] |
| TiO₂, ZnO, and Sahara desert dust | Escherichia coli (bacteria) | [181] |
|               | Pseudomonas aeruginosa (bacteria) | |
|               | Staphylococcus aureus (bacteria) | |
|               | Saccharomyces cerevisiae (F- Yeast) | |
|               | Candida albicans (F- yeast) | |
|               | Aspergillus niger (fungi) | |
| TiO₂          | Pseudokirchneriella subcapitata (algae) | [182] |
| Carbon-doped TiO₂ | Escherichia coli (bacteria) | [183] |
| TiO₂ modified with PCl₄ | Staphylococcus aureus (bacteria) | |
|               | Enterococcus faecalis (bacteria) | |
|               | Candida albicans (fungi) | |
|               | Aspergillus niger (fungi) | |
| Co and Fe ions doped TiO₂ | Cadida Albicans(fungi) | [184] |
| TiO₂          | Candida Albicans (fungi) | [185] |
| TiO₂-SiO₂     | Escherichia Coli (bacteria) | [186] |
| TiO₂          | Staphylococcus aureus (bacteria) | [187] |
|               | Methylene blue as the model pollutant | |
| TiO₂ and silver | Deinococcus geothermālis (bacteria) | [188] |
| TiO₂ and carbon | Bacillus species (bacteria) | [188] |
|               | B. subtilis | |
|               | B. cereus | |
|               | B. thuringiensis | |
|               | B. anthracis | |

4. Photocatalytic Coatings Used in Other Applications

Photocatalytic coatings are used to decontaminate the surface present contaminants for various applications in the presence of UV/solar radiation. Water/air purification, antimicrobial finishes, and self-cleaning technologies are some such applications of photocatalytic coatings. A significant number of studies have been conducted on photocatalytic coatings in recent publications, as summarized in Table 4. Cement, tiles, glass, steel, wood, and textile are some commonly used substrates for developing photocatalytic coatings. However, only a minor amount of studies have been focused on applying photocatalytic coatings on already painted substrates.[54] Also, none of the studies have been focused on applying photocatalytic coatings on pre-painted substrates for long-term outdoor applications such as roofing. Therefore, the development of photocatalytic coatings for pre-painted steel substrates for long-term outdoor applications is a novel research area with a high impact and commercial demand.

According to the chemical materials used in the formulations of Table 4, the semiconductor photocatalysts and binders can be identified as the main elements of a photocatalytic coating system. The cross-sectional view of the photocatalytic coating system has been illustrated using a multilayered model, as shown in Figure 13. Titanium dioxide (TiO₂) is widely used as the semiconductor photocatalyst in developing photocatalytic coatings. However, non-TiO₂-based photocatalysts such as ZnO, WO₂, SnO₂, CuO, ZrO₂, and CdS have also been used in some of the recent publications for developing photocatalytic coating systems as shown in Table 4.

5. Pre-Painted Steel Roofing

Painted steel roofing is widely used in residential, industrial, and commercial construction sectors compared to other diversified roofing materials due to architectural versatility, high mechanical strength, durability, recyclability, non-combustibility, lightweight nature, and nontoxicity on human health.[7] The painted steel roofing industry has grown substantially during the past decades showing the high demand in construction applications compared to other roofing materials.[56]

Steel is a microstructurally nonuniform alloy that is mainly composed of iron crystals and a minor amount of alloy elements such as carbon, manganese, silicon, copper, phosphorus, sulfur, aluminum, chromium, cobalt, niobium, molybdenum, nickel, titanium, tungsten, vanadium, and zirconium.[57] The incorporation and interaction of minor alloy elements with iron enhance the unique physical and mechanical properties of steel increasing its applications in the construction sector, tools and machinery manufacturing, automobile industry, military applications, and electrical appliances. Body-centered cubic and face-centered cubic have been identified as the two primary crystalline forms of pure iron allotropes.[58] Pure iron is known to be ductile and soft, with a high probability of slipping past iron atoms one another depending on its crystal structure. This free motion of iron atoms becomes limited due to the introduction of alloy elements (carbon), and hence the mechanical properties are improved.[59]
For example, the hardness, tensile strength, quenching behavior, and annealing requirement of steel are more favorable for practical applications compared to pure iron. Steel can be categorized into a wide range of subcategories depending on its qualitative and quantitative alloy composition. For example, carbon steel is mainly made of carbon, manganese, and silicon. Stainless steel (SS) is developed to enhance corrosion-resistant property using chromium and other alloying elements.\[7\]

Single or multiple layers of surface coatings are usually applied on steel substrates to enhance the aesthetic and functional properties depending on the applications and customer requirements. Liquid coating, powder coating, coil coating, and thermal spraying are some standard techniques for applying surface coatings on steel substrates.\[60\] The coil-coating technique can be known as the most efficient, convenient, and cost-effective method of coating up steel substrates for roofing sheet applications.\[61\] In general, the coil-coating process is automated in industrial production to cater to the high demand, continuously minimizing labor requirements. As implied by the name, coil coating is a continuous painting process in which the steel is fed in rolled coil form for painting. During the painting process, the steel roll unwinds and passes through several
coating/chemical baths. However, at the final stage, it rewinds as a completely colored steel coil with single or multiple layers of coating systems. The layered structure of a selected painted steel roofing product is shown in Figure 14 as obtained from Fletcher Steel limited.

Surface preparation is essential to enhance the quality and mechanical properties of paints that are applied to steel substrates. Water cleaning (steam cleaning and hydro blasting), solvent and chemical cleaning (emulsion cleaning, alkaline cleaning, and organic-solvent cleaning), and mechanical cleaning (blast-cleaning and flame cleaning) are some standard surface preparation techniques before applying the surface coatings. Usually, a metallic coating is then applied to protect steel from corrosion following the theory of galvanic hierarchy. As an example, a layer of aluminum and zinc alloy is used on both sides of the cleaned steel core, as shown in Figure 14. A corrosion-resistant chromate conversion coating has been applied on both the top and reverse sides as the pre-treatment.

Furthermore, a corrosion-resistant chromate-based primer layer has been applied on both top and reverse sides with an average thickness of about 7 μm ± 1 μm on the top side and 5 μm ± 1 μm on the reverse. The outer colored finish coat is usually developed with pigment-embedded acrylic or polyester coatings aiming for exterior roofing applications with an average film thickness of 18 μm ± 2 μm. Similarly, a back coat (wash coat) is also applied with the average coating thickness of 5 μm ± 1 μm with standard gray colors.

6. Challenges of Photocatalytic Coatings for Self-Cleaning Applications on Painted Steel Roofing

Even though photocatalytic coatings are a potential candidate for self-cleaning applications, such coating systems have not yet been fully developed on pre-painted steel roofing due to several reasons. The degradation of internal paint components and binders due to the activity of photogenerated reactive oxygen species ROS is a significant challenge of using photocatalytic coatings on a pre-painted substrate for a long-term outdoor application. The effect of photodegradation on binders and underneath paint components is illustrated in Figure 15. The pigment and photocatalytic particles are loosened and decline gradually from the coating surface, similar to "chalking" in conventional TiO$_2$-based pigment paintings. However, the effects of chalking have become more critical in photocatalytic coatings due to the high rate of ROS production compared with conventional paint systems. As a result, the aesthetic and functional features are weakened over time during the outdoor exposure of photocatalytic coatings when applied on a painted substrate. Accordingly, the development of a durable photocatalytic coating system on pre-painted steel is challenging for self-cleaning roofing applications.

Several challenges can be identified in developing a photocatalytic self-cleaning coating system for painted steel roofing applications. Most of the commercial photocatalysts are active only at a narrow wavelength range absorbing the
selected parts in the solar spectrum. As an example, anatase TiO$_2$ is active only in the UV-A wavelength region ($\lambda < 376$ nm) depending on its bandgap value (3.2 eV), resulting in only less than 5% absorbance of the solar flux from the incident radiation at the earth’s surface. Also, a significant portion of photogenerated charged particles ($e^+$ and $h^-$) are recombined during the photocatalytic reaction reducing the self-cleaning efficiency of photocatalytic coatings. Therefore, the photocatalytic activity needs to be enhanced further, especially for roof-coating applications due to its intended long service life and a high degree of contamination. Also, the optimization of photocatalytic activity and durability is essential but challenging due to the inverse relationship of these two parameters. The density of photogenerated ROS is increased in the enhanced photocatalyst materials resulting in a high rate of photodegradation minimizing the service life.

Self-cleaning activity and service life of photocatalytic coatings are usually studied under accelerated and simulated test conditions. The duplication of the complex solar spectrum, stresses of diurnal temperature cycling (temperature differences between daytime and nighttime), natural moisture permeation patterns, climatic parameters, atmospheric pollutant levels, and the effect of absorption/scattering of solar radiation during incident onto the earth surface are some of the challenging natural parameters that have not yet been successfully replicated in a simulated test method or testing apparatus. Therefore, probably false or contradictory conclusions can be generated from the simulated test methods when generalizing the results into real-world applications. Consequently, the performance of a novel photocatalytic coating system needs to be assessed in the presence of both simulated and natural environmental conditions as parallel studies for generating more precise, accurate, and reliable conclusions. However, such scientific studies are rare in recent publications analyzing the correlation of the results obtained from simulated and natural environmental exposure studies.

Furthermore, the analysis of performance using accelerated test methods is essential for commercial roof coating applications as it minimizes the decision-making time in industrial operations. However, the accelerated test conditions should be compatible with the natural environmental parameters to obtain precise and accurate conclusions. Most of the accelerated weathering studies of photocatalytic coatings have been conducted with standard Q-panel UltraViolet (QUV) chamber following American Society for Testing and Materials (ASTM) G154, ASTM D 4329, ASTM D 4587, and ISO 4892 standards in recent publications. However, the QUV weathering device has limitations in replicating the natural solar spectrum, surface contamination, climatic conditions, and other natural environmental parameters. The Altrac accelerated weathering racks located at Townsville, Queensland, Australia (Allunga exposure laboratory) are composed of fresnel reflecting concentrator units, fan-driven forced air droughts and programmable water spray cycles in the presence of the natural environmental conditions providing accelerated weathering conditions. However, none of the photocatalytic coating studies have been conducted under such accelerated conditions providing reliable conclusions.

The lack of scientific data on photocatalytic coatings applied to pre-painted steel substrates has become another challenge when developing a novel coating system for pre-painted steel roofing. Even though the activity of photocatalytic powders has extensively been studied in recent publications for a wide range of applications, only a minor amount of studies have been focused on photocatalysts coatings, specifically long term exterior applications. Furthermore, up to my knowledge, only one recent study has been evaluated the behavior of photocatalytic coatings...
applied on a pre-painted substrate using a TiO$_2$ based single layer coating system with a painted glass substrate.\cite{55} Accordingly, the development of photocatalytic coatings for painted steel substrates for long-term outdoor applications can be known as a novel research discipline with high demand due to a lack of scientific data. The key challenges of developing a photocatalytic self-cleaning coating system for painted steel roofing are illustrated in Figure 16 as a summary of this section.

7. Strategies for Improving the Self-Cleaning Activity of TiO$_2$ Photocatalytic Coatings

As described in Section 3, TiO$_2$-based photocatalysts seem to be a potential candidate in photo-oxidizing biological and non-biological roof contaminants. However, its photocatalytic activity needs to be further improved, especially for long-term outdoor applications. According to the bandgap value of anatase TiO$_2$, it can absorb radiation only if the wavelength is $\lambda < 376$ nm for its photocatalytic function.\cite{31} Accordingly, anatase TiO$_2$ can absorb only less than 5% of the solar flux from the incident beams at the earth’s surface.\cite{63} The reduction of photocatalytic efficacy due to the recombination of charged particles ($e^-$ and $h^+$) is another challenge in pristine TiO$_2$-based photocatalytic coatings. Most of the charged particles ($e^-$ and $h^+$), which are generated in the photocatalytic process, are easily recombined and stabilized when it is exposed to sunlight.\cite{32} As a result, self-cleaning efficiency is reduced significantly. Therefore, the strategies for enhancing the photocatalytic activity of TiO$_2$ are essential for long-term outdoor applications such as roofing.

The photocatalytic activity of TiO$_2$ can be enhanced using various methods, as summarized in the following four points. Each of these four approaches has been discussed in detail later with recent scientific findings. 1) Optimization of physicochemical properties such as particle/crystallite size, surface area, and porosity can be known as a primary method of enhancing photocatalytic activity of TiO$_2$.\cite{76–78} 2) The manipulation of surface morphology of TiO$_2$ is another method of strengthening photocatalytic efficiency. Synthesis of TiO$_2$ having various shapes such as nanoparticles, nanowires, nanotubes, and nanosheets can be known as some strategies for improving the photocatalytic activity of TiO$_2$.\cite{76,77,79} The modification of TiO$_2$ surface with different ratios of anatase–rutile heterojunctions can also be known as an efficient approach to enhancing TiO$_2$ photocatalytic activity. 3) Extending photocatalytic activity using doping technique, and 4) development of composite photocatalysts combined with other chemical substances can be known as promising techniques of enhancing the photocatalytic activity of TiO$_2$.

7.1. Optimization of Physicochemical Properties

The particle size is a critical parameter of determining the photocatalytic efficacy of a photocatalyst. The photocatalytic activity is increased when the particle size is decreased, especially when it is less than 100 nm.\cite{55,80} A high level of self-cleaning activity has been obtained with a long-lasting performance at the particle size of TiO$_2$ is 100 nm\cite{55} under both laboratory and outdoor environmental conditions. The effect of particle size of TiO$_2$ on the rate of photocatalytic degradation of methylene blue has deeply been analyzed in another study. The findings of this study have been summarized in Figure 17. The rate of methylene blue photodegradation has been increased as the particle sizes of TiO$_2$ decreased, especially when the particle size is less than 30 nm.\cite{81} In another study, the antibacterial activity has been tested against gram-positive Bacillus subtilis and gram-negative Escherichia coli (ATCC K12) by changing the particle size of the TiO$_2$ photocatalyst.\cite{82} The antibacterial activity has been increased with the reduction of primary particle size. The maximum activity has been obtained at 16–20 nm particle size.\cite{82} Large surface area, wider bandgap, and open crystal structure are the reasons to have higher photocatalytic activity in nanomaterials compared to corresponding bulk materials. Nano-TiO$_2$ can be synthesized by using different techniques such as sol–gel, spray pyrolysis, magnetron sputtered vacuum deposition, and chemical vapor deposition (CVD).\cite{83} Furthermore, nano-TiO$_2$ is available in both analytical and commercial grades for direct purchasing. However, in general, obtaining a stable homogeneous fine particle-sized nanodispersion is challenging but can be done using a
horizontal bead mill with a proper dispersing agent (e.g., γ-glycidoxypropyltrimethoxysilane) with the careful control of instrument parameters such as time, rotation speed, sample to bead ratio, and temperature.\(^{[84,85]}\)

The shape of TiO\(_2\) is another influential parameter on the photocatalytic activity over different mechanisms of adsorption of molecules and corresponding charge transfer mechanisms to molecules during the photo-oxidation reactions.

Accordingly, some studies have been conducted by changing the shape of photocatalytic TiO\(_2\) on nanometer scale, such as nanoparticles, nanowires, nanotubes, and nanosheets, to obtain enhanced photocatalytic activity.\(^{[76,77,86]}\) The dominant surface facets can also make a significant influence on photocatalytic activity.\(^{[87]}\) The facets: [110 101] have been identified as the main facet in anatase TiO\(_2\). The [1] facets become important in photocatalytic reactions due to their low Ti coordination and high ability to adsorb the reactant molecule.\(^{[86,88]}\) The surface area of TiO\(_2\) is another critical parameter of determining photocatalytic efficiency. The photocatalytic activity is increased with the increase of surface area. It has obtained higher photocatalytic activity when the surface area is around 40–60 m\(^2\) g\(^{-1}\).\(^{[89]}\)

However, the number of surface defects where the sites of electron and hole are recombined can also be increased with the surface area or with a decrease of the particle size. Therefore, these parameters need to be controlled carefully to enhance photocatalytic activity.

### 7.2. Manipulation of Anatase–Rutile Heterojunctions

In nature, TiO\(_2\) is available in three different polymorphs as anatase, rutile, and brookite.\(^{[90]}\) The photocatalytic activity of anatase phase TiO\(_2\) is relatively higher than the other two polymorph forms. However, the activity can significantly be enhanced when anatase TiO\(_2\) nanoparticles are dispersed with rutile phase TiO\(_2\) to form anatase–rutile heterojunctions at the surface of TiO\(_2\) particles. The quantitative composition of anatase–rutile phases is powerfully influential on photocatalytic efficiency. The photocatalytic activity of different compositions of anatase–rutile-mixed phases is compared in Figure 18. Accordingly, the highest photocatalytic activity has been obtained at the ratio of 84%...
anatase and 16% rutile,\textsuperscript{[91–93]} which is known as P25 TiO$_2$ in the trade name.

The mechanism of synergistic electron transfer at the anatase–rutile heterojunctions has been identified as the main reason for having a higher photocatalytic activity in P25 TiO$_2$. Mainly the photoexcited electrons in the valence band of the rutile phase are transferred into the conduction band of the rutile phase due to its relatively shorter bandgap (3.0 eV) compared to the anatase phase (3.2 eV) as shown in Figure 19.\textsuperscript{[94]}

The excited electrons in the conduction band of rutile are then transferred into the conduction band of the anatase phase over a synergistic electron relation pathway at the anatase–rutile interfacial heterojunctions. Accordingly, the photogenerated holes in the anatase valance band are transferred into the valence band of rutile for charge balance in the anatase phase energy levels. Thus, the rate of charged particle recombination is low in P25 TiO$_2$ due to the surface presence of anatase–rutile heterojunctions. Hence, a higher portion of charge particles remains active for the photo-oxidation reactions of roof contaminants. Furthermore, the charge separation is faster in P25 due to the relatively shorter bandgap of rutile.

### 7.3. Addition of Doping Agents

Doping is referred to as the addition of a minor amount of metallic or nonmetallic substances into TiO$_2$ is a well-known technique to obtain enhanced photocatalytic activity. The introduction of a dopant into the TiO$_2$ matrix cause changes in its optical bandgaps, as shown in Figure 20. The bandgap engineering due to the introduction of dopant material has narrowed down the geometric gap of both metal and nonmetal doped-TiO$_2$ by extending the active wavelength from the UV to UV and visible regions. The extended activity in the visible light region is useful for long-term outdoor applications such as roofing as the visible light region covers the central part of the solar spectrum and then can perform under low illumination of lighting conditions even in the absence of sunlight. Furthermore, the impurity dopant elements can act as a site of trapping the photogenerated holes by delaying and reducing the rate of charge particle recombination. Similarly, the number of charge carrier sites can also be increased due to the introduction of impurity elements/compounds resulting in higher photocatalytic activity in doped-TiO$_2$ materials.\textsuperscript{[95–97]} The dopants introduce additional energy levels that act as a site of trapping electrons or holes allowing more carriers that can diffuse to the TiO$_2$ surface for the photocatalytic reaction.

The photocatalytic activity of doped-TiO$_2$ is dependent on the type of dopants used, the concentration of dopants, and the synthesis pathways. Reactive sputtering, plasma techniques, ion-implantation, CVD, and sol–gel are some standard methods of synthesizing doped TiO$_2$.\textsuperscript{[98,99]} Some transition metals (Pt, Au, Pd, Cr, Co, V, Rh, Ru, Ag, Fe, Cu or bimetallic) and metal oxides (NiO, CuO, or RuO$_2$) have widely been used as dopants in recent studies.\textsuperscript{[76,100–102]} It has been reported that the Cr-, Co-, V-, and Fe-doped TiO$_2$ has shown a higher photocatalytic activity compared to the pure anatase-TiO$_2$ in both UV and visible light regions.\textsuperscript{[103]} Similarly, in another study, it has been found that the doping of TiO$_2$ with nonmetal elements such as N, C, B, and S has shown red-shifts in the TiO$_2$ absorption spectrum by shifting to the visible light region.\textsuperscript{[63]}

Similarly, the changes in photocatalytic activity depending on the type of dopant used are compared in Table 5 based on the methylene blue (MB) degradation rate constant values of various doped TiO$_2$ materials from 20 recent studies. The doped photocatalysts have been classified as single-metal-doped, single-nonmetal doped, and multiple dopants for the convenience of analysis. The interval plots which are generated for single-metal doped and single-nonmetal-doped TiO$_2$ photocatalysts are compared in Figure 21. Accordingly, the average photocatalytic
activity of metal-doped photocatalysts seems to be higher than that of nonmetal-doped materials. Furthermore, a considerable variation and noticeable overlapped region can be observed in the activity levels of both metal-doped and nonmetal-doped TiO$_2$. However, the usage of metal-doped TiO$_2$ has become limited in industrial applications due to the manufacturing challenges resulting due to low thermal instability. High sensitivity toward dopant concentration as the activity of metal-doped TiO$_2$ is decreased after a certain dopant concentration and a higher probability of acting as recombination centers due to the localized d-states presence in metal-doped TiO$_2$. Furthermore, the high cost of metal-doped TiO$_2$ has become another critical limitation of applying for roofing due to its large surface area requirement. Therefore a nonmetal doped commercial photocatalysts, can be recommended to obtain enhanced photocatalytic activity in practical applications.

Also, doping and sensitization of semiconductors by graphene has become another interesting research area to improve the photocatalytic efficacy of conventional photocatalysts. A significant amount of hierarchical 2D graphene nanosheets-supported semiconductor photocatalysts have also been widely synthesized and applied in different photocatalytic fields. Strategies such as improving the electrical conductivity, increasing electrocatalytic active sites, strengthening interface coupling, fabricating micro/nanoarchitectures, constructing multijunction nanocomposites, enhancing photo stability of semiconductors, and utilizing the synergistic effect of various modification strategies of graphene have been widely considered in recent research methodologies. Hierarchical and graphene-based photocatalysts are used in advanced applications such as thermal catalysis, separation, and purification processes to solar cells.

As shown in Figure 21, most of the doped-TiO$_2$ photocatalysts have a higher photocatalytic activity than 100% anatase TiO$_2$ ($K' = 0.0157$ min$^{-1}$) and P25 ($K' = 0.0221$ min$^{-1}$). However, in some cases, the photocatalytic activity can be lower in doped materials compared to its corresponding undoped state due to reasons such as acting of dopant site as a charged particle recombination centers. Furthermore, the photocatalytic efficacy can be varied even with the same dopant type depending on synthesis parameters and dopant concentration. Therefore, the type of dopant, concentration of dopants, and synthesis technique need to be appropriately controlled to obtain enhanced self-cleaning activity in doped materials. Furthermore, the cooperation of multiple dopants can be used to obtain enhanced photocatalytic activity up to a significant level, as shown in Table 5. However, the usage of multiple dopants has not yet been successfully developed for large-scale commercial applications, mainly due to the high cost of these materials.

### 7.4. Combining with Inorganic Additives

The photocatalytic activity of TiO$_2$ is increased significantly in the presence of SiO$_2$ or polysiloxanes in the coating composition. The refractive index of the TiO$_2$–SiO$_2$ film is reduced in the presence of SiO$_2$ compared to pure TiO$_2$ film. Therefore, the extent of light absorption in composite TiO$_2$–SiO$_2$ film is increased with increased photocatalytic activity. Furthermore, the P1H effect of pure TiO$_2$ film is gradually converted back to its original hydrophobic state in the absence of light. However, the composite TiO$_2$–SiO$_2$ films exhibit enhanced superhydrophilicity properties even in dark conditions. Therefore enhanced self-cleaning activity is expected from TiO$_2$–SiO$_2$-based coatings compared to pristine TiO$_2$. The higher self-cleaning activity, cost-effectiveness, relative resistance toward photodegradation, availability, non-toxicity, transparency, colorlessness, and process stability are some other favorable physicochemical properties of TiO$_2$–SiO$_2$ composites for commercial self-cleaning applications. The photocatalytic activity of different TiO$_2$–SiO$_2$ composites is compared in Table 6

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**Table 5.** Methylene blue photo-oxidation rate constant values of doped TiO$_2$ based photocatalysts.

| Single-metal dopants | Single-nonmetal dopants | Multiple dopants |
|----------------------|-------------------------|------------------|
| Dopant | $K'$ [min$^{-1}$] | References | Dopant | $K'$ [min$^{-1}$] | References | Dopant | $K'$ [min$^{-1}$] | References |
|-------|------------------|-------------|-------|------------------|-------------|-------|------------------|-------------|
| Au    | 0.064            | [189]       | F     | 0.014            | [190]       | Au/CuO | 0.0748           | [191]       |
| Pd    | 0.044            | [192]       | P     | 0.045            | [110]       | Yb, N  | 0.0091           | [193]       |
| Fe    | 0.033            | [110]       | C     | 0.0018           | [194]       | Fe,Ge,P| 0.128            | [110]       |
| Gd    | 0.072            | [110]       | B     | 0.0291           | [195]       | N,S    | 0.0301           | [111]       |
| Al    | 0.0143           | [196]       | N     | 0.00498          | [193]       | –      | –                | –           |
| Ti    | 0.0439           | [197]       | F     | 0.0024           | [198]       | –      | –                | –           |
| Mn    | 0.0328           | [199]       | P     | 0.034            | [112]       | –      | –                | –           |
| Nb    | 0.0058           | [200]       | N     | 0.00213          | [201]       | –      | –                | –           |

**Figure 21.** Comparison of photocatalytic activity in metal- and nonmetal-doped TiO$_2$ based on the values in Table 5.
Table 6. Comparison of photocatalytic activity of TiO$_2$–SiO$_2$ composites.

| Description | Technique | Model | Photocatalytic activity [$k^0 (\text{min}^{-1})$] | References |
|-------------|-----------|-------|-----------------------------------------------|------------|
| Teardrop-shaped core–shell SiO$_2$/TiO$_2$ nanoparticles | Sol–gel | [202] | 0.03475 | [113] |
| Raspberry-Like SiO$_2$–TiO$_2$ nanoparticles | Layer by layer deposition | | 0.1056 | [114] |
| Titania nanoparticles with mesoporous silica nanoparticles | Ultrasonication mixing | Copyright (2019), with permission from American Chemical Society | 0.071 (SiO$_2$ 0%) | 0.103 (SiO$_2$ 20%) | 0.117 (SiO$_2$ 40%) | 0.144 (SiO$_2$ 60%) | 0.032 (SiO$_2$ 80%) | [118] |
| Nano titania Particles Embedded in Mesoporous Silica | Sol–gel | Not given | 0.322 (TiO$_2$/SiO$_2$ molar ratio 1) | 0.293 (TiO$_2$/SiO$_2$ molar ratio 1.5) | 0.255 (TiO$_2$/SiO$_2$ molar ratio 2.4) | [115] |
| Mesoporous TiO$_2$–SiO$_2$ hybrid | Sol–gel | Copyright (2019), with permission from The Chemical Society of Japan (CSJ) | Increased activity at 4 % TiO$_2$ (w/v) and decreased activity at 10 % (w/v) | [202] |
| Nano-TiO$_2$-coated SiO$_2$ microsphere | Co-grinding followed by calcination | Copyright (2019), with permission from Creative Commons Attribution License | Higher activity | [203] |
The photocatalytic activity is significantly influenced by the ratio of TiO2 and SiO2 in the coating composition. It has been found that the photocatalytic activity is increased with SiO2 concentration up to a certain level and decreased again after an optimum TiO2:SiO2 ratio.115,118,119 The changes in photocatalytic activity of TiO2-based photocatalytic coatings having different TiO2–SiO2 ratios are summarized in Table 6 from recent publications. Interestingly, the self-cleaning activity has increased at 4% TiO2 (w/v) in a TiO2–SiO2 mesoporous hybrid but decreased at 10% (w/v) TiO2 concentration in the same hybrid system. The reduction of photocatalytic activity at higher TiO2 concentrations can be explained due to the decrease in useful porous volume in the composite matrix and thus creating difficulties in accessing photoactive sites.119 Moreover, it has been found that the photocatalytic activity has been suppressed significantly when the TiO2 particle surface is coated with SiO2,120 which may limit access to photoactive sites. Therefore, the ratio of TiO2:SiO2 and the structural arrangement of TiO2 and SiO2 in the composite matrix become critical parameters in photocatalytic coatings to obtain enhanced self-cleaning activity. These parameters can be controlled by controlling the synthesis parameters and the experimental sequence. Sol–gel synthesis,121 dielectric barrier discharge (DBD) plasma treatments,122 atmospheric pressure plasma jet,123 CVD,124 magnetrons sputtering,125 and hydrothermal synthesis126 are some standard methods of synthesizing TiO2–SiO2 composites.

### 7.5. Non-TiO2-Based Photocatalysts

Several studies have been focused on the photocatalytic activity of non-TiO2-based photocatalysts for different applications in recent literature, as summarized in Table 7. The distribution of MB degradation rate constants of these non-TiO2 photocatalysts is shown in Figure 22. Accordingly, the vast majority of non-TiO2 photocatalysts have shown relatively less photocatalytic activity compared to TiO2-based P25 photocatalysts.127–129 However, the photocatalytic activity of non-TiO2-based photocatalysts can be increased by using the doping technique and synthesizing composite materials. Interestingly it has been found that some other metal oxides, such as WO3, SnO2, and ZnO, can also exhibit the “PIH” similar to TiO2.130 A smaller bandgap has been obtained with some non-TiO2-based photocatalysts such as V2O5,131 Bi2WO6,127 BiVO4,132 Bi25Ge2O39,133 SnO2,134 WO3,135 CdS,1107 and Fe2O31136 compared to TiO2 (3.2 eV). Therefore, visible light activity can be expected from these photocatalysts having a smaller bandgap even without any further modifications. Also, cadmium sulfide (CdS)-based photocatalysts have been studied considerably due to its strong visible light absorption and high electronic charge transport properties.117 Development of cocatalysts has also become a high-demand research area in semiconductor photocatalytic studies. As an example, multiple strategies such as increasing interfacial interactions, improving electrocatalytic activity, enhancing charge separation, and increasing light harvesting.
can be applied to improve the photocatalytic efficacy of co-catalysts. Various cocatalysts, such as biomimetic, metal-based, metal-free, and multifunctional ones, have been extensively studied in recent publications.

However, according to the market revenue values of different photocatalytic materials, TiO$_2$ is still used as the most common photocatalyst for commercial applications due to its cost-effectiveness, availability, stability, and higher activity. Moreover, most of the recent non-TiO$_2$-based photocatalysts are known to be costly due to the usage of expensive rare metals and hence minimize the applications for roof coatings due to their large surface area requirements. Furthermore, some of the non-TiO$_2$-based photocatalysts have shown stability issues and environmental concerns. Therefore TiO$_2$-based semiconductor photocatalysts seem to be the first choice for large-scale commercial applications.

### 8. Strategies for Improving the Service Life of the Photocatalytic Coatings

Obtaining a durable photocatalytic coating on a painted substrate for long-term outdoor applications is challenging due to the photo-oxidation of binders and internal paint components due to the power of photogenerated ROS. Therefore, different strategies have been used in recent studies to enhance the overall service life of photocatalytic coatings applied on painted substrates, as summarized in Figure 23. Surface modification of photocatalytic particles is also used to control the photodegradation rates of binders and internal paint components to obtain long-lasting performance. Incorporation of an additional ROS resistant (non-oxidizable) binders and paint auxiliaries

- EG: Polysiloxanes, Fluoropolymers
- Incooperation of an intermediate protective layer
- Optimization of the film thickness < 1 um
- Optimization of the concentration of photocatalyst
- Surface modification of photocatalytic particles

Figure 22. Methylene blue photo-oxidation rate constant values of non-TiO$_2$-based photocatalysts corresponding to 7.

![Figure 22](image-url)

Figure 23. Strategies for obtaining a durable photocatalytic coating.

![Figure 23](image-url)
protective layer in between the underlying paint and photocatalytic top layer is another efficient approach of reducing photodegradation of underlying paint components that have been discussed in the later of this chapter.

Furthermore, the optimization of TiO$_2$ concentration via the optimization of TiO$_2$ to binder ratio is highly important to minimize the photodegradation of paint components. The TiO$_2$ concentration can also be controlled by optimizing the film thickness. It has been found that the optimum results can be obtained when the film thickness is less than 1 μm.$^{[142]}$ Accordingly, the strategies used in recent studies for enhancing the service life of photocatalytic coatings have been summarized in Table 8. However, none of the studies have been consolidated all the strategies explained in Figure 23 in a single study with detailed scientific analysis.

The introduction of an additional intermediate protective layer in between the underlying paint and the photocatalytic top layer, as shown in Figure 13 can be known as an efficient approach to enhancing the service life of photocatalytic coatings applied on a painted substrate. This additional protective layer minimizes the diffusion of photogenerated ROS from the top most photocatalytic layer into subsequent underlying paint layers due to its resistance towards photo-oxidation.$^{[143]}$ Accordingly, polysiloxanes and fluorocarbon polymers have been used as the primary component in the protective layer compositions.$^{[143,144]}$ The patent literature confirms the application of an additional protective layer in between the photocatalytic top layer and the underlying paint layer by using colloidal silica and 2-[methoxy (olygoethylenoxy)propyl]heptamethyltrisiloxane as the organosilicon surfactant.$^{[145]}$ Similarly, silicates, silicone, or alkyl alkoxy silane-based materials have been used in several other patents as the protective layer composition to enhance the service life of photocatalytic coatings via the minimization of photodegradation of internal paint components.$^{[145,146]}$

Some other studies have confirmed the application of a SiO$_2$ barrier layer for TiO$_2$-based photocatalytic films on polycarbonate substrates for long-lasting performance.$^{[147–149]}$

Encapsulation or the surface modification of photocatalytic particles by forming a protective shell around the photocatalytic particles is another approach of controlling the diffusion of ROS into an internal paint matrix to minimize photodegradation of internal paint components. However, the photocatalytic activity is significantly reduced in these protective shell-type structures of photocatalyst particles due to the limitation in accessing active sites on photocatalytic particles when during the photo-oxidation reactions of surface contaminants.$^{[150]}$

Polysiloxanes are widely used in photocatalytic coating formulations due to high photochemical stability, non-toxicity, and enhanced surface hydrophilicity of the extended Si-O (-Si-O-Si-O-Si-O-) polymer backbone.$^{[151]}$ The hydrophilic nature of Si-O (452 kJ mol$^{-1}$ at 298 K)$^{[152]}$ and stability of the Si-O group are mainly determined by the photochemical stability of polysiloxanes against photodegradation ROS.$^{[153]}$ The dissociation energies of different chemical bonds that are mostly present in polysiloxanes have been compared with organic chemical bonds in Table 8 as evidence for the high stability of polysiloxanes.$^{[152]}$

Polysiloxanes are synthesized using single or multiple silane precursors (alkoxysilanes and organosilanes) generally to obtain homopolymers, copolymers, or terpolymers depending on the requirement. Silane precursors are classified into four classes as Q, T, D, and M depending on the number of directly attached oxygen atoms on each silicon atom representing quaternary, tertiary, di, and mono substitution.$^{[154]}$ respectively, shown in Figure 24. As an example, tetraethylorthosilicate and MTMS are referred to as Q-type and T-type silane precursors, respectively, as they have four and three oxygen atoms directly bonded to the centric Si atom. The types of silane precursors and synthesis parameters need to be chosen carefully, as they determine the physicochemical properties, degree of polymerization, geometric distribution of polymer chains, and the crosslinking density of the synthesized polysiloxane material. The service life of self-cleaning coatings systems is determined accordingly.

The polymerization of silane is initiated by hydrolysis in the presence of an acid/base catalyst forming the corresponding silanol product, as shown in the following general chemical reaction. The value of x (x = 0, 1, 2, or 3) represents the degree of hydrolysis in a single silane molecule determined by the reaction conditions.$^{[154]}$

$$R_x^4Si(OH)_{(4–x)} + (4 – X)H_2O \rightarrow R_x^4Si(OH)_{(4–x)}$$

$$+ (4 – X)ROH \ (9)$$

The resultant silanols can again be re-esterified with alcohol molecules depending on their concentration, as shown in the following chemical reaction. The R$^2$ can probably be similar to R in the previous step. As an example, the rate of re-esterification is increased in the presence of alcoholic solvents reducing the overall rate of polysiloxanes production.$^{[55]}$

$$R_x^4Si(OH)_{(4–x)} + (4 – X)R^2OH$$

$$\rightarrow R_x^4Si(OH)_{(4–x)} + (4 – X)ROH \ (10)$$

The unreacted silanols can then be condensed into polysiloxane under two mechanisms, as shown in the following chemical reaction by producing either water or alcohol by-products depending on the nature of the silane precursors.

$$\sim Si – OH + HO\sim Si \sim Si – O – Si \sim + H_2O \ (11)$$

$$\sim Si – OH + RO\sim Si \sim Si – O – Si \sim + ROH \ (12)$$

However, the hydrolysis followed by condensation of a silanol precursor is complicated and can generate a series of products depending on the experimental parameters. As an example, the products that can be formed due to hydrolysis, followed by condensation of MTMS, are shown in the cascading reactions of Figure 25.

This cascading reaction scheme can also be transformed into a numerical representation of three integer values, as shown in Figure 26, respectively, the number of alkoxys (RO-), hydroxyl (-OH), and siloxy(SiO-) groups that have been substituted in a silane is represented by the first three integer values. As an example, MTMS is represented by “300.” Furthermore, it has been reported that the base-catalyzed hydrolysis followed by condensation is preferably undergone through 300 and 003 pathways. In contrast, acid-catalyzed hydrolysis followed by condensation has taken place, over 300 and 030 pathways.
Table 8. Summary of recent studies of extending the service life of photocatalytic coatings.

| Binder system          | Precursor materials                                           | TiO$_2$ ratio [w/w%] | Film thickness | MB oxidation rate constant [k (min$^{-1}$)] | Durability measures                              | References |
|------------------------|---------------------------------------------------------------|-----------------------|----------------|--------------------------------------------|-------------------------------------------------|------------|
| Silane based sol–gel   | Tetraethylorthosilane (TEOS) Methyltrimethoxysilane (MTMS)  | P25                   | 33–45%         | 0.5–1.4 μm                                  | 70% gloss retention after 1800 h                 | [55]       |
|                        | Tetrabutylorthotitanate (TBOT) TiO$_2$                        |                       |                | >120 nm                                    | 13.2 (10%), 33.1 (15%)                           | [124]      |
|                        | Fluorosilane 1 H, 1 H, 2 H, 2 H- perfluoroctyltrioxyisilane   |                       |                | Ethanol-1.36%                               | Not given                                       | [208]      |
|                        | 3,3,4,4,5,5,6,6,7,7,8,8, tridecafluorooctyl 1 H, 1 H, 1     |                       |                | Fluorosilane – 1.36 %                        | Not given                                       | [209]      |
|                        | triethoxysilane trimethoxy(3,3,3-trifluoroethyl)               |                       |                |                                             | Not given                                       | [210]      |
|                        | Fluoropolymer Isocyanate/ hexamethoxydimethylmelamine based  |                       |                |                                             | Not given                                       | [211]      |
|                        | Styrene-acrylic Phthalocyanine Tetraacrylic Acids              |                       |                |                                             | Not given                                       | [212]      |
|                        | Polydimethylsiloxane (PDMS)-Grafted-SiO$_2$/TiO$_2$ PDMS-SiO$_2$(s) TiO$_2$ |                       |                |                                             | Not given                                       | [213]      |
|                        | Fluorinated/(meth)acrylic latex P25                            |                       |                |                                             | Not given                                       | [214]      |
|                        | Commercial materials have been used                            |                       |                |                                             | Not given                                       | [34]       |
|                        | Polyurethane Titanium isopropoxide Sol-gel titanium (IV)      |                       |                |                                             | Not given                                       | [121]      |
|                        | Acrylic binders with nanofibrillated cellulose (NFC)           |                       |                |                                             | Not given                                       | [141]      |

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The two matrices that are shown in Figure 25 and 26 express the possibility of forming a wide range of products even for a single reactant molecule (MTMS) without considering the formation of an extended polymer network and the impact of neighboring chemical species. Accordingly, formation reactions of a polysiloxane are complicated even for a single monomer when synthesizing a homopolymer. Therefore, the structure and formation reaction of a copolymer with two silane precursors (e.g., MTMS–TEOS co-polymer) becomes further complicated but can be represented in a general formula. Also, the kinetics of silane polymerization reactions are dependent on various parameters such as water: silane ratio, catalyst, nature of the silane, temperature, pH, solvent, ionic strength, and silane: solvent ratio. Accordingly, the physiochemical properties and physical nature (sol, gel, or silsesquioxanes) of a polysiloxane are influential by all these parameters. Therefore, the synthesis of polysiloxane materials for photocatalytic self-cleaning coating systems needs to be designed carefully.

Table 9. Comparison of dissociation energies (at 298 K) and lengths of chemical bonds present in polysiloxanes and conventional binders.\(^{[152]}\)

| Chemical bond | Bond dissociation energy [kJ mol\(^{-1}\)] | Bond length [pm] |
|---------------|------------------------------------------|-----------------|
| Si-O          | 452                                      | 163             |
| C-O           | 358                                      | 143             |
| C-Si          | 318                                      | 186             |
| C-C           | 346                                      | 154             |
| Si-Si         | 222                                      | 233             |

Figure 24. Classification of silanes based on the chemical structure, where \(R\) is an alkyl and \(R_1\) is an organic group. Reproduced with permission.\(^{[154]}\) 2022, MDPI.

Figure 25. Cascade reaction of hydrolysis followed by condensation of MTMS. Reproduced with permission.\(^{[168]}\) 2022, Taylor and Francis.
9. Challenges of Performance Evaluation in Photocatalytic Self-Cleaning Coatings for Painted Steel Roofing Applications

The self-cleaning activity and service life assessments are the two significant factors of determining the level of performance of photocatalytic coatings obtained in this study, along with developing an efficient and durable self-cleaning coating system for painted steel roof application. The methods that can be used to evaluate the performance of photocatalytic coatings are summarized in Figure 27 based on the recent studies of photocatalytic coatings. Three main test methods can be identified from the current scientific publications as useful tools for assessing the self-cleaning activity of photocatalytic coatings under accelerated test conditions in laboratory environments using model pollutants and test conditions. Analysis of the rate of photo-oxidation of methylene blue as a model pollutant (ISO 10678-2010), analysis of the antimicrobial activity of photocatalytic coatings using critical microorganisms (ISO 27447-2009), and evaluation of changes in surface hydrophilicity upon UV irradiation can be identified as the standard test methods to assess self-cleaning activity in the laboratory.

However, none of the studies have been compared to the self-cleaning activity systematically using the standard grading test methods under natural environmental conditions in parallel to the evaluation methods with model pollutants and accelerated...
under UV irradiation is driven by
\[
\text{MB} + 102\text{OH}_2 \rightarrow 16\text{CO}_2 + 3\text{NO}_3^- + \text{SO}_4^{2-} + 6\text{H}^+ + 57\text{H}_2\text{O}
\]

where \( \text{MB} \) is the molar concentration of methylene blue in the presence of \( \text{TiO}_2 \) under UV irradiation. The reversible adsorption of MB on the photocatalytic \( \text{TiO}_2 \) surface agrees with the Langmuir behavior.\(^{158} \) The hydroxyl radicals (OH\(^{-}\)), which are generated in the presence of UV radiation, attack the MB ring sulfur atom, initiating the oxidation reaction. Accordingly, the MB ring is opened after a series of reactions destroying the structure of chromophore units (extended conjugation), gradually reducing the color intensity as shown in the following chemical reaction.\(^{159} \) This color reduction is quantified by UV-vis spectros-
copy as a function of time. The overall chemical reaction agrees with the pseudo first-order rate Equation (18).\(^{159} \)

\[
\text{MB}^{\text{aq}} + 102\text{OH}_2 \rightarrow 16\text{CO}_2 + 3\text{NO}_3^- + \text{SO}_4^{2-} + 6\text{H}^+ + 57\text{H}_2\text{O}
\]

The Langmuir–Hinshelwood kinetic model is used to explain the photo-oxidation rate \( (r) \) of MB using the following rate equation,\(^{159} \) where \( k \) is the rate constant of MB photo-oxidation and \( K \) is the equilibrium constant of MB adsorption.

\[
r = -\frac{d[\text{MB}]}{dt} = \frac{kK[\text{MB}]}{1 + K[\text{MB}]} \quad (14)
\]

The above equation can further be simplified into the following rate equation since \( K[\text{MB}] \ll 1 \).

\[
r = -\frac{d[\text{MB}]}{dt} = kK[\text{MB}] \quad (15)
\]

Hence

\[
\frac{d[\text{MB}]}{[\text{MB}]} = -kKdt \quad (16)
\]

Accordingly, the following pseudo-first-order rate equation is obtained, where \([\text{MB}])\) is the molar concentrations of methylene blue at time \( t \), \([\text{MB}_o])\) is the molar concentrations of methylene blue at time 0, and \( k' \) is the pseudo-first-order rate constant (typically expressed in \( \text{min}^{-1} \)). The value of \( k' \) is widely used to quantify and compare the photocatalytic self-cleaning activity of semiconductor powders and thin films.

\[
\ln \left\{ \frac{[\text{MB}]_t}{[\text{MB}]_0} \right\} = -k't \quad (17)
\]

The ratio of molar concentration values of MB can be replaced using the UV-vis absorbance values according to the Beer–Lambert law, as shown in the following equation. Where \([A])\) is the molar absorbance of methylene blue at time \( t \), \([A]_0 \) is the molar absorbance of methylene blue at time 0. The value of \( k' \) can be calculated from the intercept of the graph between \( \ln ([A]/[A]_0) \) and time.\(^{131} \)

\[
\ln \left\{ \frac{[A]_t}{[A]_0} \right\} = -k't \quad (18)
\]

The self-cleaning activity of photocatalyst powders and coatings applied on pre-painted steel substrates are analyzed using the photo-oxidation reaction kinetics of aqueous MB buffered at \( \text{pH} \) 6 and temperature 20 \(^\circ\)C following the standard ISO 10678:2010 test method. The recommendations of Mills et al. and Chen et al. on these test methods further validate the results of this test more precisely to generate reproducible results.\(^{31,160} \)

The reaction kinetics of MB photo-oxidation (ISO 10678-2010) has widely been used in photocatalytic studies as a tool for measuring the self-cleaning activity as summarized in Table 10. The magnitude of the rate constant value of MB photo-oxidation depends on several other testing parameters such as the concentration of MB stock solution, the volume of MB, \( \text{pH} \) of the medium, purity of MB, stirring and diffusion, light intensity, and irradiation time as can be seen in Table 10. Therefore, a cross-comparison of rate constant values can only be done after careful consideration of all these test parameters.\(^{31,160} \) It has been found that the reproducibility of the ISO 10678-2010 test results is relatively low within a lab (9.2%) and between labs (30.6%).\(^{160} \) However, accurate and reproducible results have been obtained in recent photocatalytic studies with careful control of the above testing parameters. Furthermore, this test method is explicitly designed to assess the self-cleaning activity of dissolved organic pollutants in aqueous mediums. However, roof contaminants can be existed in the aqueous and nonaqueous medium in roofing environments, depending on the climatic parameters. Furthermore, the co-relation of photo-oxidation kinetics on MB and other contaminants such as gaseous pollutants, soil, and microorganisms has not yet been studied in a recent publication. Therefore the generalization of MB photo-

oxidation kinetic results in real-world performance needs to be analyzed separately elsewhere.

The service life of photocatalytic coatings has been evaluated by comparing the changes in chemical, morphological, optical, and mechanical properties before and after exposure to different weathering conditions. The changes of physicochemical properties of photocatalytic coatings over time and methods of assessing the rates of photodegrading have been summarized in Figure 28. Spectroscopic techniques such as attenuated total reflector-fourier transformed infrared spectroscopy (ATR-FTIR), energy dispersive spectroscopy (EDS), and solid-state nuclear magnetic resonance spectroscopy (SSNMR) can be used to analyze the chemical composition changes that have occurred during weathering due to photodegradation. Microscopic techniques such as atomic force microscopy (AFM), SEM, and
Morphological and optical changes
- Gloss reduction
- Colour change
- Surface roughness change

Chemical composition changes
- Functional groups
- Elemental composition

Mechanical charges
- Chalking
- Flaking and peeling
- Blistering

Figure 28. Effect of photo-degradation on changes in physicochemical properties of photocatalytic coatings. Reproduced with permission.© 2022, Elsevier.

Table 10. Effect of testing parameters on photocatalytic activity of TiO$_2$ based on the MB photo-oxidation reaction kinetics.

| Photocatalyst                          | Composition | Concentration | Particle size [nm] | Value of $k' [\text{min}^{-1}]$ | Light intensity                  | References |
|----------------------------------------|-------------|---------------|-------------------|-------------------------------|----------------------------------|------------|
| P25 TiO$_2$                            | A=84% R=16% | TiO$_2$-0.030 g MB-150 mL of 4.9 × 10$^{-5}$ mol L$^{-1}$ | A=29 R=55 | 0.0221 | Photon flux: 6.5 m W cm$^{-2}$ 100 W 365 nm | [31] |
| Anatase (A) TiO$_2$                     | A=100%      | TiO$_2$-0.030 g MB-150 mL of 4.9 × 10$^{-5}$ mol L$^{-1}$ | A=10 R=10.2 | 0.0157 | Photon flux: 6.5 m W cm$^{-2}$ 100 W 365 nm | [31] |
| Rutile (R) TiO$_2$                     | R=100%      | TiO$_2$-0.030 g MB-150 mL of 4.9 × 10$^{-5}$ mol L$^{-1}$ MB solution | R=57 | 0.0003 | Photon flux: 6.5 m W cm$^{-2}$ 100 W 365 nm | [31] |
| Anatase–brookite–rutile TiO$_2$        | A=84.6 B=12.8 R=2.6 | MB-200 mL of 32 mg L$^{-1}$ TiO$_2$-0.6 g L | A=18.2 B=12.3 R=43.2 | 0.0553 | 100 W high-pressure mercury lamp | [215] |
| TiO$_2$/PANI (polyaniline)             | A=100%      | TiO$_2$-0.25 × g MB-100 mL 10 mg L | 5–10 nm | 0.00184 (pure TiO$_2$) 0.0006 (TiO$_2$/PANI) | UV light | [216] |
| Gold nanoparticles                     | Not given   | 50 mL (10 mg L$^{-1}$) aqueous solution of MB 1 mg of catalyst | 10–50 nm | 0.1758 | UV light | [217] |
| Zinc oxide/graphene oxide              | C=65.73, O=29.67, Zn=4.61% | MB-50 mL from intensity 2.1 solution | Mean----22 nm | 0.254 | UV-light (wavelength 365 nm, distance 100 mm, power 40 W) | [218] |
| Ultrasmall W$_6$O$_{49}$ NPs          | 100%        | 50 mL (10 mg L$^{-1}$) aqueous solution of MB was taken and 10 mg of the prepared catalyst | 5–7 nm | 0.176 (10 ppm) 0.145 (20 ppm) 0.098 (50 ppm) | Not given | [219] |
| Ti$^{3+}$ self-doped TiO$_2$           | 100%        | 0.06 g of sample was dispersed into 100 mL MB solution (2 × 10$^{-5}$ mol L$^{-1}$) | NG | 0.0439 | 300 W Xe arc lamp | [220] |
| Silver–zinc oxide (Ag–ZnO) nanostructures | 100% | 10 mg–MB—10 ppm | 10–50 nm | 0.059668 0.02527 (control) | Natural sunlight intensity 97 000 l× | [221] |
| Teardrop-shaped core–shell SiO$_2$/TiO$_2$ nanoparticles | 100% | 10 mg L | 20 nm | 0.03475 | Xenon lamp (300 W) | [113] |
optical microscopy can be used to analyze the morphological changes of the photocatalytic coatings due to photodegradation. The changes in optical properties as a function of weathering time is assessed using gloss retention and color change measurements according to the standard L, a, b color coordinates. The changes in mechanical properties can be measured according to the AS/NZS 1580 standard to understand the effect of photodegradation of internal paint components.

Attenuated total reflection (ATR) is a widely used analytical technique in photocatalytic coating studies to service the life and rate of photodegradation. It can introduce samples without any special sample preparation such as the conventional KBR pellet disk preparation. An evanescent wave is generated and passed through the exposed sample due to the total internal reflection of the IR beam inside the ATR crystal, as shown in Figure 29. The depth of penetration (Dp) into a sample can be with a magnitude of 0.5–2 μm, depending on the incident beam wavelength, incidence angle, and the indices of refraction for the ATR crystal and the sample.[163] Accordingly, only a limited depth profile can be assessed in ATR-FTIR studies in photocatalytic self-cleaning coating studies. Therefore, the photo-degradation of underneath paint layers may not be counted in the results especially when considering multi-layer coating models. Accordingly, the results need to be generalized only after careful evaluation of film thicknesses of each layer in the photocatalytic coating systems. The refractive index of the ATR crystal has to be higher than the refractive index of the sample being analyzed to obtain the total internal reflection and hence the materials such as diamond, germanium, KRS-5, and zinc selenide are used to produce ATR crystals due to its higher refractive indices.[162]

The standard QUV test conditions (ISO 4892) are widely used in photocatalytic coating studies to study the influence of weathering.[44,55,163] The QUV testing chamber is composed of two types of stimulated UV radiation sources, namely UV-B and UVA-340. The radiation intensity spectrums of these light sources have been compared with the solar spectrum in Figure 30.[164] Accordingly, a considerable variation is expected in the energy spectrums of these stimulated lights compared to the natural sunlight, especially when the wavelength is greater than 360 nm. Therefore, the replication of natural weathering conditions inside a QUV chamber is questionable, especially in the studies of TiO2-based photocatalysts as the TiO2 bandgap (370 nm), visible, and IR light regions are not covered in the energy spectrums of UV-B and UVA-340 lights. The Xenon arc lamps are also widely used in photocatalytic studies to stimulate the natural solar spectrum.[164,165] The energy spectrums of the xenon arc lamp and the natural solar spectrum are compared in Figure 30. Even though the Xenon arc lamps are more closely duplicated the solar spectrum, it has not been fully replicated the natural solar spectrum. Furthermore, none of the artificial weathering devices have been developed yet to stimulate natural environmental parameters such as natural contaminants to match qualitative and quantitative compositions, the effect of climatic parameters, atmospheric pollutant and humidity levels, stresses of diurnal temperature cycling, and interrelationships among these natural parameters.[165]

The service life evaluation of photocatalytic coatings has been carried out under natural exposure conditions in some of the recent studies in parallel to the laboratory-based accelerated test methods. However, none of these studies have been focused on painted steel substrates for long-term outdoor applications. Furthermore, the detailed scientific analysis is limited to the natural weathering of photocatalytic coatings, comparing the changes in chemical, morphological, optical, and mechanical properties of the coatings over time. Similarly, the correlation between the results associated with simulated and natural weathering conditions has rarely been studied in recent publications.

The self-cleaning activity and service life of photocatalytic coatings are widely studied using accelerated and simulated test conditions. The replication of natural environmental parameters in simulated test conditions is a challenge due to several reasons. The stresses of diurnal temperature cycling (daytime–nighttime temperature differences), duplication of the complex solar spectrum, effects of atmospheric moisture permeation, climatic parameters, atmospheric pollutant levels, and the absorption and scattering of sunlight by atmospheric constituents during reaching of solar radiation onto the earth surface are some such challenging parameters in simulating accelerated test conditions.[64] Accordingly, the results generated from simulated and accelerated test methods may sometimes lead to false or contradictory conclusions when generalizing into real-world applications.[65] Therefore, it is important to analyze the self-cleaning activity and service life of the developed photocatalytic coating systems in the presence of the natural environmental parameters in parallel to the results obtained under simulated test conditions as a measure of success.

The self-cleaning activity and service life of photocatalytic coatings can be analyzed under accelerated natural environmental and weathering conditions using the Altrac exposure racks of the Allunga exposure laboratory (Townsville, Queensland, Australia). The exposure parameters are designed according to the specifications of ASTM D1014-18: standard practice for conducting exterior exposure tests of paints and coatings on metal substrates. The “Altrac” exposure racks are composed of fresnel reflecting concentrator devices as shown in Figure 31 and generate accelerated weathering conditions using the natural solar spectrum. The principle and mechanism of the fresnel reflecting concentrator units have been discussed in a separate publication.[166] The Altrac exposure racks have a fresnel-like

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**Figure 29.** The function of attenuated total reflector unit in FTIR. Reproduced with permission.[170] © 2022, e-Century Publishing Corporation.
array of ten mirrors focused onto a target test zone on a sample. These units are rotated during the daytime, tracking the movement of the solar direction. A specially designed pyranometer sensor is used to measure the radiation in the target area.

The surface temperatures of the exposed samples are regulated with fan-driven forced-air draughts and programmable water spray cycles simulating natural environmental conditions. Altrac exposure racks have not been used much in recent photocatalytic coating studies, but it will be a profound technique in future studies to generate more accurate and reliable results for accelerated natural weathering conditions.

10. Conclusion and Suggestions for Future Work

The types of critical roof contaminants common to painted steel can be classified as biological and non-biological pollutants. Cladosporium species, Bacillus species, Cyanobacteria, Actinobacteria, Epicoccum nigrum, and Teratosphaeriaceae species have been identified as the most dominant organisms on painted steel roofing. The photocatalytic activity of TiO₂ is a promising technology of photo-oxidizing these biological and non-biological roof contaminants in the presence of sunlight, water, and oxygen for self-cleaning applications. Photogenerated hydroxyl radicals initiate the photocatalytic self-cleaning reaction resulting in a complete oxidation of organic and other oxidizable pollutants over time. Photo-induced
hydrophilicity achieved through photo-generated oxygen vacancy sites of TiO$_2$ further enhances the self-cleaning activity due to easy wash off hydrophilic pollutants and repellent property of hydrophobic pollutants. Furthermore, TiO$_2$ has become the first choice selection for commercial applications due to its cost-effectiveness, higher activity, favorable physicochemical properties, and non-photo corrosion behavior compared to non-TiO$_2$ based photocatalysts.

However, a number of challenges have been identified in this technology when applying on painted steel roofing for real-world applications. Unselective photo-oxidation of internal paint components, limited activity of photocatalytic materials in a narrow wave length range, reduced photocatalytic efficiency due to charge particle recombination, inverse relationship of photocatalytic activity and service life, lack of any co-relation records between simulated/accelerated test methods and natural environmental exposure performance, difficulties in replicating natural solar spectrum and other environmental conditions in accelerated test methods and lack of scientific data specifically about painted steel roofing can be identified as some such challenges. Therefore, these challenges need to be carefully analyzed to develop efficient and durable photocatalytic self-cleaning technologies for painted steel roofing applications in future research. It will be important and demanding to address these challenges in future research aiming to remediate fouling on painted steel roofing to improve the quality of roof harvested rainwater.

Photocatalytic efficacy needs to be maximized in roofing applications due to its higher density of pollutant exposure over a relatively long period in outdoor atmospheric conditions. P25 (84% anatase and 14% rutile) is found to be the most active form of TiO$_2$ due to the synergistic effect at the anatase–rutile hetero-junctions. Surface manipulation of TiO$_2$ particles is an effective approach to improving self-cleaning efficiency. Optimization of physicochemical properties such as particle size, polymorphic form are other useful tools to obtain higher self-cleaning efficiency. The photocatalytic activity is high when the particle size is less than 100 nm. The highest activity has been obtained when particle size becomes less than 30 nm. The doping technique is used to re-engineer the energy levels of photocatalytic materials, resulting in an extended photocatalytic activity into the visible light region. The analysis of ten recent research papers confirms that the activity of metal-doped TiO$_2$ is higher than nonmetal-doped TiO$_2$. However, the metal-doped photocatalysts have some practical limitations, and hence nonmetal-doped TiO$_2$ can be recommended for roofing applications to enhance photocatalytic activity into visible light range. Furthermore, the addition of inorganic additives and usage of specific non-TiO$_2$-based photocatalyst have shown an improvement in photocatalytic self-cleaning efficiency. Therefore, these techniques can be used in future research to enhance the photocatalytic self-cleaning activity for roofing applications. Also, the coupling with co-catalysts/co-doping techniques, incorporation of graphene chemistry in developing composite heterogeneous photocatalysts, and studies on synthesizing hierarchical photocatalysts are important areas for future studies to improve photocatalytic efficacy.

The higher activity of photocatalytic coatings negatively influences the coating service life due to photodegradation of internal paint components in presence of the activity of photogenerated ROS. Therefore, the development of a durable and efficient photocatalytic coating for long-term self-cleaning applications is challenging. Some strategies can be identified from recent scientific studies to enhance the service life of photocatalytic coatings. Incorporation of non photo-oxidizable binder systems, incorporation of an intermediate protective layer, maintaining the film thickness of less than 1 μm, optimization of photocatalytic concentration can be known as promising methods of obtaining durable photocatalytic self-cleaning coatings. However, all these strategies have not been analyzed deeply and systematically in current studies targeting the enhancement of service life of photocatalytic coatings. Therefore, a systematic evaluation of the effect of the protective layer, film thickness, photocatalyst concentration, and binder type will be an important research area to optimize the photocatalytic activity and service life.

Different performance evaluation methods have been published in recent studies of photocatalytic coatings, but none of them has been designed explicitly on roofing applications. Therefore, the current test methods need to be used and interpreted for self-cleaning roofing applications with a proper understanding and careful consideration. Furthermore, none of the simulated weathering devices have become successful yet to replicate natural weathering cycles. Comparatively, Attract accelerated exposure racks (Allunga exposure lab – Queensland – Australia) can be used in future studies to derive more reliable results for natural weathering and environmental exposure studies. The results of environmental exposure studies need to be conducted as a measure of success in parallel to accelerated and stimulated test methods. Moreover, only a negligible amount of studies has been undertaken to study the correlation between laboratory test methods and real-world performance in recent scientific studies. Therefore conducting research on analyzing the co-relation between laboratory test results and real-world performance would be very useful for future studies in the field. Also, the development of a statistical model to co-relate laboratory performance, accelerated test results, and real-world performance will be a high-demand research area for future studies.

Furthermore, the photo-oxidation mechanism and by-products that can be generated from various pollutants have not yet been analyzed deeply in current research. Therefore it will be important to study the photo-oxidation mechanism and kinetics of different pollutants in future studies to understand the environmental impact of overall self-cleaning reaction.

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Conflict of Interest

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