Photocatalytic Antimicrobial Coating as Self-Disinfecting Surface for Defeating Various Contagious Diseases: A Review

N. K. M. Salleh, F. Aziz* & S. S. Mohtar

Advanced Membrane Technology Research Centre (AMTEC), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310, UTM Johor Bahru, Johor, Malaysia


ABSTRACT

Surface contamination with pathogenic microorganisms such as *E. coli* and *S. aureus* may lead to the spread of numerous diseases such as pneumonia and sepsis. The most common sources of surface contamination are human contamination and the environment, which includes air, dust, and water. Conventional cleaning and disinfection practices are not sufficient to ensure the safety and not environmentally friendly to use. It has been proposed that a visible light active photocatalytic antimicrobial coating on the indoor surface can successfully control this increasing threat. Photocatalysis is recognized as one of the promising approaches and metal oxides as photocatalyst have showed significant potential antibacterial agents against a variety of bacteria. Cuprous oxide (Cu₂O) has been recognized as potential visible light active photocatalyst for antimicrobial applications due to its large bandgap. The current review highlights the antimicrobial properties of various Cu₂O-based photocatalyst and their potential use as coatings. This review article will introduce the related parameters in Cu₂O-based photocatalyst applications as antimicrobial coatings in order to provide better understanding on achieving excellent performance in photocatalytic disinfection. This review may be beneficial in guiding photocatalyst research for antimicrobial applications in the visible light region.

*Keywords: Antimicrobial, coating, photocatalyst, visible-light, cuprous oxide*

1.0 INTRODUCTION

The presence of bacteria that can cause diseases in humans, such as *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*), has been a serious health concern for decades. Bacterial growth on surfaces, particularly disease-causing microorganisms, can lead to the spread of a number of diseases. Meanwhile, bacteria residues that survive death might emit endotoxins that cause typhoid and cholera, resulting in secondary contamination [1]. Furthermore, the most recent Coronavirus Disease (COVID-19) outbreak has resulted in an infection that can be contracted by inhaling the virus or touching contaminated surfaces. Cleaning, sanitization and disinfection of surfaces are a regular practice nowadays in order to control the spread of these diseases. Chemical disinfectants are applied to disinfect contaminated surfaces in the majority of situations. However, chemical disinfectants are also difficult to handle and can be harsh at times, due to their unpleasant odour and chemical content. In addition, disinfectants must be used correctly to achieve the desired results. Chemical disinfectants are also known to produce toxic disinfection by-products, according to evidence [2]. Thus, there is an urgent need to
develop self-disinfecting surfaces to control the spread of these diseases through contaminated surfaces. Antimicrobial coatings have been acknowledged as one of the innovative approaches, in addition to proper cleaning and disinfecting processes used to eliminate microorganisms. Antimicrobial coating works by integrating active substances on surfaces to inhibit the growth of bacteria that comes into contact with the treated surfaces [3]. Various kinds of antimicrobial coatings were explored, such as spraying silver and copper to be the surface coatings in killing those microorganisms [4]. These metals, however, are unsafe for humans. Hence, the interest in antimicrobial coatings studies has shifted to photocatalytic technology. Photocatalytic technology has been proven to be one of the most "green" and successful environmental remediation solutions. This technology has also been proven effective in various applications, including biological contamination, self-cleaning buildings, deodorizing, and antibacterial action [5]. Photocatalytic surface coating is one of the significant methods to remove pathogens from frequently touched surfaces [6]. Photocatalysis is a type of artificial photosynthesis that uses green, environmentally friendly chemistry to solve energy and environmental problems [7]. A photocatalyst is a compound that generate UV or visible light and uses it to decompose various substances, including organic compounds and microorganisms. Metal oxides, also known as semiconductors, have been explored as photocatalysts for their potent antimicrobial properties owing to their unique photocatalytic properties [2].

Cuprous oxide (Cu2O) has been recognized as one of the most promising visible light active photocatalyst due to its narrow bandgap (2.0-2.4 eV), environmentally friendly, low cost, and excellent absorption in visible light region [8]. In recent years, the application of Cu2O as visible-light active photocatalyst has gained attention [9]–[11]. However, despite its unique qualities, Cu2O has a significant limitation due to its narrow bandgap; the photogenerated electrons could quickly recombine with the holes, leading to a low quantum efficiency. Various studies have been carried out in order to implement effective measures to improve Cu2O photocatalytic activity and stability to overcome the limitation.

This article highlights in detail basic photocatalytic mechanism, offers a brief insight on photocatalyst application, and factors affecting Cu2O-based photocatalytic antimicrobial coating for indoor applications to present a clear image of photocatalytic antimicrobial process.

2.0 PHOTOCATALYSIS

Photocatalysis occurs when a light source interacts with the surface of a photocatalyst and accelerates the chemical reaction. Photocatalysis has recently been recognized as an effective green solution technology for antimicrobial applications. Over the decades, the application of photocatalytic antimicrobial coatings has been thoroughly evaluated for inactivation of various types of microorganisms. Other than antimicrobial application, environmental photocatalysis, including water disinfection, organic contaminant removal, air purification, and hazardous waste remediation, has gained a lot of attention [5]. The photocatalytic process is divided into three stages: (1) photoinduced charge carrier generation, (2) charge carrier
Photocatalytic Antimicrobial Coating as Self-disinfecting Surface

separation, and distribution to the photocatalyst surface, and (3) oxidation and reduction reactions on the photocatalyst surface [12].

In general, photocatalysis occurs when a photocatalyst (PC) is exposed to light. Irradiation of light with the energy equal to or greater than the band gap energy of the semiconductor photocatalyst light, excites the electrons in the photocatalyst, resulting in the formation of an electron conduction band. In the first stage, the valence band and the conduction band, respectively, form photo-generated holes and electrons. As a result, these photoinduced charge carriers combine with water or dissolved oxygen to produce reactive oxidising species like OH and O₂, which decompose contaminants into smaller molecules whilst inactivating microorganisms. Figure 1 illustrates the general mechanism of photocatalytic antimicrobial disinfection. The following steps describe the main reaction that occurs in photocatalysis.

Figure 1 Illustration of photocatalytic mechanism [13]

1) Photoexcitation
Photocatalyst + $h_v \rightarrow e_{CB}^- + h_{VB}^+$

2) Charge carrier trapping of $e^-$:
$e_{CB}^- + O_2 \rightarrow O_2^{2-}$

3) Charge trapping of $h^+$:
$h_{VB}^+ + H_2O \rightarrow \cdot OH + H^+$

4) Photodegradation of microorganism:
Microorganisms/Organic compounds + $\cdot OH + O_2 \rightarrow CO_2 + H_2O$

It is important to note that photocatalytic processes have been investigated and are becoming identified for their capabilities in antimicrobial applications. The list of photocatalytic antimicrobial applications is identified in Table 1.
Table 1 List of Photocatalytic Antimicrobial Applications

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Major findings</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag NPs</td>
<td>Cotton fiber displayed long-lasting antibacterial activity against pathogens such as S. aureus, E. coli, and Candida albicans.</td>
<td>[14]</td>
</tr>
<tr>
<td>TiO$_2$ NPs doped with Cu$_2$O NP</td>
<td>shows self-cleaning property under direct sunlight. -showed great antimicrobial activity against Gram-positive and Gram-negative bacteria.</td>
<td>[15]</td>
</tr>
<tr>
<td>ZnO</td>
<td>The coatings prevented bacterial growth and biofilm formation on surfaces.</td>
<td>[16]</td>
</tr>
<tr>
<td>HAp, TiO$_2$ composite</td>
<td>The antimicrobial activity tests revealed that the composite films inhibited Gram positive and Gram-negative bacteria effectively.</td>
<td>[17]</td>
</tr>
<tr>
<td>Bi$_2$O$_3$, TiO$_2$ Bismuth tungstate</td>
<td>$Bi_2O_3$ outperformed bismuth tungstate and TiO$_2$ in bacterial inactivation tests under visible light.</td>
<td>[18]</td>
</tr>
<tr>
<td>TiO$_2$ doped SiO$_2$</td>
<td>-the antimicrobial activity increased as the TiO$_2$ content increased under UVA and visible-light irradiation. -combination of TiO$_2$ and SiO$_2$ significantly improved the utilization of visible light</td>
<td>[1]</td>
</tr>
</tbody>
</table>

2.1 Cu$_2$O as Photocatalyst for Indoor Antimicrobial Applications

Metal oxides such as TiO$_2$ and Cu$_2$O has been widely used as a photocatalyst has been recognized their potential for antimicrobial applications. Cu$_2$O is a p-type semiconductor with a narrow band gap of 2.2 eV that has a lot of potential as a photocatalyst and excellent absorption in visible light region [20]. Studies has been conducted in order to explore the antimicrobial potential of Cu$_2$O and develop efficient method to improve the photocatalytic activity of Cu$_2$O. The formation of composites has been proposed as one of the methods to improve the photocatalytic performance of Cu$_2$O [21]. The formation of composites offers the possibility of promoting charge carrier mobility, resulting in the generation of an internal electric field. It thus improves charge carrier separation, resulting in improved Cu$_2$O performance as a photocatalyst. [22] has prepared Cu$_2$O-Ag nanocomposites with improved durability and bactericidal activity. Figure 2 shows SEM images of morphologies and microstructures of pure Cu$_2$O and Cu$_2$O-Ag. The image showed Cu$_2$O still had spherical microstructures after Ag deposition, while the surfaces of the microspheres became substantially rougher. The result also proved that the Cu$_2$O-Ag nanocomposites exhibits highly long-term sterilization against selected microorganisms within 14 days.
Photocatalytic Antimicrobial Coating as Self-disinfecting Surface

[15] prepared Cu2O/TiO2 composite to impregnate in cotton fabric to produce a fiber with increased thermal stability, UV protection, and antibacterial activity. Figure 3 represents a SEM image of pristine cotton fabric with a smooth surface structure of the microstructure, whereas after coating the fabric with Cu2O/TiO2, the surface reveals roughness with the deposited layer. The antimicrobial activity of TiO2,Cu2O/TiO2 with different concentration are tested against Gram-negative bacteria (*Escherichia coli, Kleissella pneumonia*) and Gram-positive bacteria (*Staphylococcus aureus*). TiO2 showed no effect against all bacteria meanwhile 9% of Cu2O/TiO2 showed highest antimicrobial activity against all bacteria. Thus, the formation of Cu2O/TiO2 composites does increased the antimicrobial activity.

Understanding the microorganisms’ inactivation process is critical for the successful development of novel composites for photocatalytic disinfection mechanisms [23]. The photocatalytic performance of a photocatalyst strongly depends on its electronic band structure and band gap energy [24]. According to Yemmireddy and Hung [2], the generated ROS such as hydroxyl (OH), superoxide (O2-) radicals, and...
hydrogen peroxide (H$_2$O$_2$) can be effectively utilized to completely mineralize organic compounds, including bacterial cells, into CO$_2$ and H$_2$O.

Cell walls and membranes are important barriers for bacterial resistance to the external environment as well as for maintaining the bacterium’s natural shape [25]. Different adsorption pathways for photocatalysts, Gram-positive (G+) and Gram-negative (G-) bacteria are produced by cell membrane components. The G+ bacteria indicate the presence of a single peptidoglycan polymer layer that accounts for approximately 80% of the cell wall composition, with the rest being fats and lipids [23]. The structure of Gram-positive and Gram-negative bacteria are illustrated in the following diagrams (Figure 4). The thickness of the peptidoglycan layer and the presence or absence of the outer lipid membrane are two essential factors that cause Gram-positive and Gram-negative organisms to exhibit different visibility properties. Hence, the ability of bacteria to hold stains depends on the structure of the cell wall. Bacteria are the most commonly studied model organisms in understanding disinfection mechanisms and evaluating the photocatalytic efficiency of composites. Bacterial metabolism disorder damages bacterial cell membranes and causes oxidative stress, eventually leading to bacterial cell death. Bacterial metabolic pathways are not isolated, but are rather part of the complex activity of living cells. However, the exact mechanisms of microbial destruction are poorly understood, but currently accepted mechanisms include oxidative stress induction, metal ion release, and non-oxidative mechanisms [25]. The antimicrobial mechanisms of photocatalytic activity disruption are exhibited by various photocatalytic semiconductors.

Figure 4 Schematic diagrams illustrating the difference in the bacteria cell wall composition [26]

Excess reactive oxygen species (ROS) are produced as a result of the redox process, resulting in oxidative stress induction. Cellular oxidative
stress has been identified as a key contributor to the changing in permeability of the cell membrane, which can result in bacterial cell membrane damage. By reducing oxygen molecules, different types of ROS can be produced, such as $O_2^-$, OH, H$_2$O$_2$, and O$_2$. The generated ROS will cause less acute stress reactions and can be neutralized by antioxidant systems such as superoxide enzymes and catalase, whereas CO$_2$ and OH will cause acute microbial death [25]. Besides, these ROS will also penetrate the cell membrane to kill bacteria. The generation of ROS degrades the active components that are responsible for maintaining the normal morphological and physiological functions of the microorganism. Negatively charged O$_2^-$ and OH radicals can be maintained on the cell surface and do not penetrate into the intracellular regions of bacteria, whereas H$_2$O$_2$ can pass through the cell membrane. Nonetheless, it is uncertain which reactive species would significantly contribute to bacterial inactivation. Because different photocatalytic systems employ different reaction mechanisms, hence it is critical to investigate the radical species formed during the process and determine which radical species is crucial in the photocatalytic process [11]. Scavenger experiments and electron spin resonance (ESR) are used to investigate the major ROS involved in the photocatalytic inactivation process.

2.2 Parameters Affecting the Cu$_2$O-based Photocatalytic Antimicrobial Coating

The photocatalytic performance of antimicrobial coatings against microorganisms is a very complicated process. Therefore, in order to exhibit the efficacy of photocatalytic antimicrobial coatings, there are a few parameters that affect the performance which are the catalyst loading and the method of coating. These parameters are considered as they will affect the photocatalytic coating performance against microorganisms. These operating parameters are important in order to develop an ideal photocatalytic antimicrobial coating.

2.2.1 Effects of Catalyst Loading

The effect of catalyst loading is essentially important in photocatalytic activity as it has a significant impact on the efficiency of the photocatalytic antimicrobial process. Several studies have found that increasing the
concentration of the catalyst improves the disinfection process. [27] synthesized ZnO-Ag nanoparticles to improve the photocatalytic activity against E. coli under solar irradiation.

The result presented in Figure 6 showed that a catalyst loading 0.25 mg mL\(^{-1}\) demonstrated highest increase in bacterial inactivation.

![Figure 6](image)

**Figure 6** Effect of ZnO concentration on the inactivation of E. coli under solar light [27]

The highest inactivation of *E. coli* observed at a catalyst loading of 0.25 mg mL\(^{-1}\) could be attributed to the high absorption of sunlight, which results in the formation of a large amount of reactive oxygen species (ROS) that interacts with the bacterial mass. [1] prepared TiO\(_2\)-doped SiO\(_2\) to evaluate the antimicrobial properties under UV-light and visible light irradiation. Figure 7 shows the antimicrobial images of TiO\(_2\) doped SiO\(_2\) with different TiO\(_2\) contents on *E. coli* under different types of irradiations (UV light and visible light). The results showed that the bacteria reduction had significantly increased as the TiO\(_2\) doping content was increased from 1.5% to 4.4%. Meanwhile, as the TiO\(_2\) doping percentage increased to more than 4.44%, the antibacterial ratio gradually increased. These findings show that increasing the TiO\(_2\) doping content improves antimicrobial activity which related to ROS generation from antibacterial hybrid materials under various light irradiation conditions. The efficacy of the inactivation process can be hindered by loading the catalyst beyond its optimal mass.
Figure 7 Antimicrobial image of the TiO2@SiO2 hybrid materials with different TiO2 contents on E. coli: (a–h) UVA irradiation and (A–H) visible-light irradiation [1]

[28] developed Fe-doped TiO2 thin films with different doping levels on glass substrates. Figure 8 shows the surface morphology of TiO2 thin films and 0.1% Fe-doped TiO2 films. The results show that thin and dense needle-like nanoparticles appeared on the surface of the films, forming deeper valleys with voids and peaks with protrusions between the nanoparticles after Fe-doping. For antibacterial activity, the optimal dopant ratio is 0.1% Fe. After 3 hours of visible light irradiation, a 0.1% Fe-doped TiO2 film was observed to be highly effective in inactivating E. coli.

Figure 8 3D AFM images of (a) bare TiO2 films and (b) 0.1 at% of Fe-doped TiO2 film [28]
Optimizing catalyst loading is important for specific disinfection processes to avoid excessive catalyst loading as the catalyst reaches a saturation point, where the rate of the reaction remains constant even as the catalyst concentration is further increased. That is because an increase in catalyst loading may result in a light blockage. This will reduce photocatalytic efficiency and results in wasted catalyst [29].

2.2.2 Effects of Coating Method

Photocatalytic activity is greatly influenced by the coating method and by the substrate nature [30]. The coating method will influence the coating thickness on the substrate. As in case of photocatalytic self-cleaning surfaces, it is critical to determine the catalyst layer’s thickness that exhibits the highest photocatalytic activity and transparency in the visible spectral range, in order to provide the required self-cleaning activity while maintaining the visual appearance of the coated surface [31]. The coating method will also significantly affect the coating morphology and optical properties; hence the photocatalytic activity depends on the coating parameters that are controllable. Depending on the method used, thin films with different surface structures can be obtained, which affects their properties [32]. The most common method is dip-coating, allowing for the production of thin films with thicknesses ranging from a few nanometres to several micrometres. Coating materials have various deposition mechanisms that must be investigated in order to reveal their benefits and drawbacks for the desired application. Many coating methods are available, but only a few are among the most effective and applicable. Although coating processes used provide the required benefits, they have limitations that reduce their reliability. There are several influencing parameters for a successful coating deposition on a substrate, including deposition materials, substrate materials, material form, and deposition methods. Coating layers vary in thickness, microstructure, and functionality depending on the substrate materials and deposition method used [33], [34] used hydrothermal treatment and dip coating procedures to immobilize TiO\(_2\) film on the surface of activated carbon fibres (ACFs) and investigate the effects on the microstructure of coated fibres. The results show that hydrothermal treatment provided many advantages in obtaining high-performance TiO\(_2\)/ACFs photocatalyst compared to dip-coating. Figure 9 shows SEM images of samples (a) dip coating and (b) hydrothermal after ultrasonic vibration. Dip coating shows a large number of TiO\(_2\) fragments flaking away from ACFs. Meanwhile, hydrothermal treatment also shows the TiO\(_2\) flakes being stripped. However, the extent of destruction was significantly less than that shown by dip coating, indicating that hydrothermal sample’s binding property is better compared to that of dip coating sample. The result shows that the coating methods affect the microstructure, adhesion properties and photocatalytic activity.
prepared TiO$_2$ thin films fabricated on the substrate with different solution concentrations and various deposition cycles to investigate the thickness effect on the photocatalytic activity. Table 2 summarizes the morphological and structural properties of TiO$_2$ thin films prepared from different solution concentrations and spray cycles. We can see the highest roughness of films increases to 2.6 nm at 15 spray cycles with concentration 0.1 M. The photocatalytic findings indicate that the 190 nm-thick TiO$_2$ film produced from the 0.1 M solution using 7 spray cycles had the finest grain structure and the highest photocatalytic activity, resulting in 94% stearic acid degradation in 180 minutes under UV-A light. Based on the studies, we can conclude that the coating method will affect the photocatalytic activity influenced by the coating thickness and the surface morphology. However, the optimum thickness that exhibits the highest photocatalytic activity may vary depending on the types of the substrate studied. Hence, technologies for coating fabrication must be efficient, reliable, economical, and resource-efficient, and be able to coat surfaces with various profiles and shapes.

Table 2 Summary of the morphological and structural properties of TiO$_2$ thin films [31]

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>TTIP Concentration in Solution (M)</th>
<th>Deposition Time (min)</th>
<th>Deposition Rate (nm min$^{-1}$)</th>
<th>Thickness (nm)/SEM</th>
<th>RMS (nm)/AFM</th>
<th>Mean Crystallite Size (nm)/XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.1</td>
<td>2.9</td>
<td>22.4</td>
<td>65</td>
<td>1.60</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>8.7</td>
<td>19.0</td>
<td>170</td>
<td>1.60</td>
<td>45</td>
</tr>
<tr>
<td>15</td>
<td>0.1</td>
<td>21.75</td>
<td>20.9</td>
<td>455</td>
<td>2.60</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>2.9</td>
<td>17.2</td>
<td>50</td>
<td>0.80</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>0.2</td>
<td>8.7</td>
<td>23.6</td>
<td>205</td>
<td>1.10</td>
<td>35</td>
</tr>
<tr>
<td>15</td>
<td>0.2</td>
<td>21.75</td>
<td>29.2</td>
<td>635</td>
<td>1.60</td>
<td>40</td>
</tr>
</tbody>
</table>

3.0 CONCLUSION

Photocatalytic antimicrobial coatings or self-disinfecting surfaces are effective solution for reducing bacteria contamination on surface which are known to transmit disease. Cu$_2$O-based have been proposed as photocatalysts for visible-light active antimicrobial coating applications. This paper
discusses the applications, mechanisms, and recent research on the use Cu$_2$O-based as a photocatalyst for antimicrobial coatings. This paper focuses on catalyst loading to determine the optimum catalyst loading and layer thickness depending on the coating method while developing Cu$_2$O-based photocatalytic antimicrobial coatings that will affect photocatalytic antimicrobial activity. Taking these factors into account, visible-light active Cu$_2$O-based photocatalytic antimicrobial coatings presents new opportunities and critical provisions that should be pursued for commercial uses and wide applications.

ACKNOWLEDGEMENT

This work was supported by the Japan International Cooperation Agency (JICA) under Special Program for Research Against Covid-19 (SPRAC) Aun/Seed-Net [Grant number: RJ130000.7351.4B610].

REFERENCES


Doi: 10.3390/nano9071011.


Doi: 10.3390/catal11081001.


Doi: 10.1016/j.apsusc.2019.02.163.


Doi: 10.1016/j.apcatb.2018.08.020.


