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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

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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 (Cu_2O) 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 Cu_2O-based photocatalyst and their potential use as coatings. This review article will introduce the related parameters in Cu_2O-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, sanitation 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

* Corresponding to: F. Aziz (email: farhanaaziz@utm.my)
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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 (Cu_2O) 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 Cu_2O as visible-light active photocatalyst has gained attention [9]–[11]. However, despite its unique qualities, Cu_2O 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 Cu_2O 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 Cu_2O-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 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 O_2, 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.

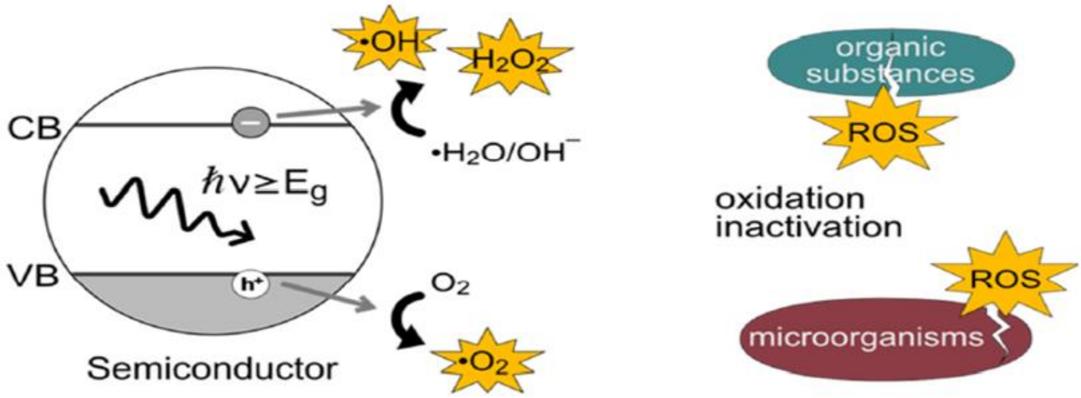

Figure 1 Illustration of photocatalytic mechanism [13]

1)Photoexcitation

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

2)Charge carrier trapping of e^-:

$e_{CB}^- + O_2 \rightarrow O_2^{\bullet -}$

3)Charge trapping of h^+:

$h_{VB}^+ + H_2O \rightarrow \bullet OH + H^+$

4)Photodegradation of microorganism:

Microorganisms/Organic compounds + $\bullet OH + O_2 \rightarrow CO_2 + H_2O$

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

Photocatalyst	Major findings	Ref.
Ag NPs	Cotton fiber displayed long-lasting antibacterial activity against pathogens such as S. aureus, E. coli, and Candida albicans.	[14]
TiO_2 NPs doped with Cu_2O NP	shows self-cleaning property under direct sunlight. -showed great antimicrobial activity against Gram-positive and Gram-negative bacteria.	[15]
ZnO	The coatings prevented bacterial growth and biofilm formation on surfaces.	[16]
HAp, TiO_2 composite	The antimicrobial activity tests revealed that the composite films inhibited Gram positive and Gram-negative bacteria effectively.	[17]
Bi_2O_3, TiO_2 Bismuth tungstate	Bi_2O_3 outperformed bismuth tungstate and TiO_2 in bacterial inactivation tests under visible light.	[18]
TiO_2 doped SiO_2	-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	[1]
Bi_2WO_6/TiO_2 composite	-the Bi_2WO_6/TiO_2 coated polyester fabric shows good self-cleaning property	[19]

2.1 Cu_2O as Photocatalyst for Indoor Antimicrobial Applications

Metal oxides such as TiO_2 and Cu_2O has been widely used as a photocatalyst has been recognized their potential for antimicrobial applications. Cu_2O 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_2O and develop efficient method to improve the photocatalytic activity of Cu_2O. The formation of composites has been proposed as one of the methods to improve the photocatalytic performance of Cu_2O [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_2O performance as a photocatalyst. [22] has prepared Cu_2O-Ag nanocomposites with improved durability and bactericidal activity. Figure 2 shows SEM images of morphologies and microstructures of pure Cu_2O and Cu_2O-Ag. The image showed Cu_2O still had spherical microstructures after Ag deposition, while the surfaces of the microspheres became substantially rougher. The result also proved that the Cu_2O-Ag nanocomposites exhibits highly long-term sterilization against selected microorganisms within 14 days.

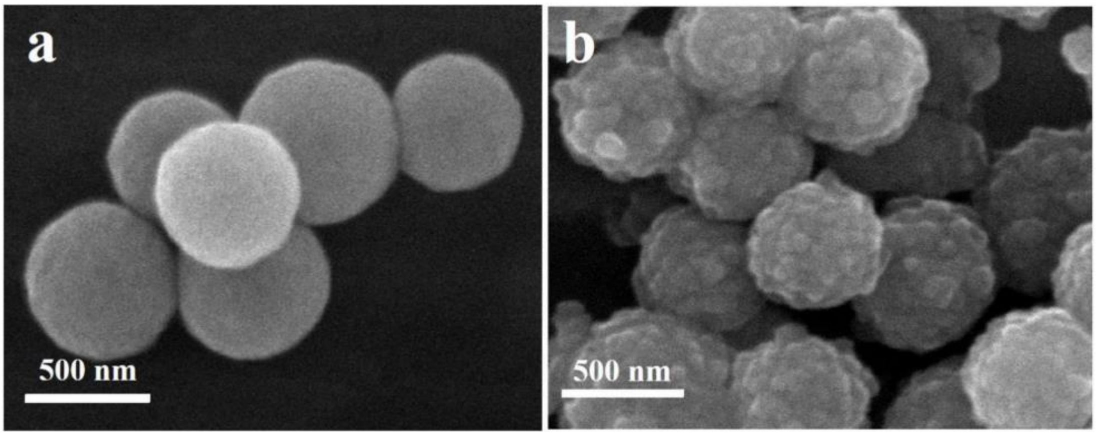

Figure 2 SEM image of Cu2O microspheres (a) and Cu2O-Ag microspheres (b) [22]

[15] prepared Cu_2O/TiO_2 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 Cu_2O/TiO_2, the surface reveals roughness with the deposited layer. The antimicrobial activity of TiO_2,Cu_2O/TiO_2 with different concentration are tested against Gram-negative bacteria (*Escherichia coli, Kleissella pneumonia*) and Gram-positive bacteria (*Staphylococcus aureus*). TiO_2 showed no effect against all bacteria meanwhile 9% of Cu_2O/TiO_2 showed highest antimicrobial activity against all bacteria. Thus, the formation of Cu_2O/TiO_2 composites does increased the antimicrobial activity.

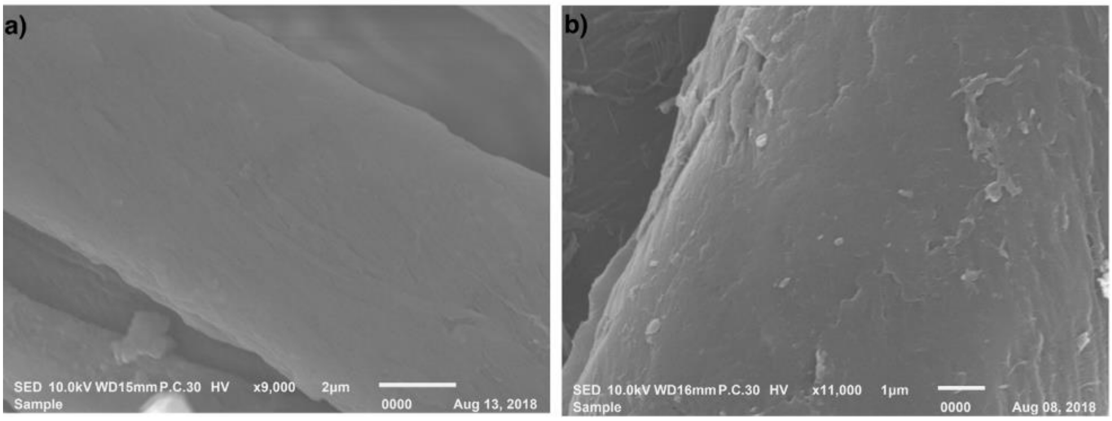

Figure 3 SEM image of a) uncoated pristine cotton fabric b) coated pristine cotton [15]

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 (O_2-) radicals, and hydrogen peroxide (H_2O_2) can be effectively utilized to completely mineralize organic compounds, including bacterial cells, into CO_2 and H_2O.

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.

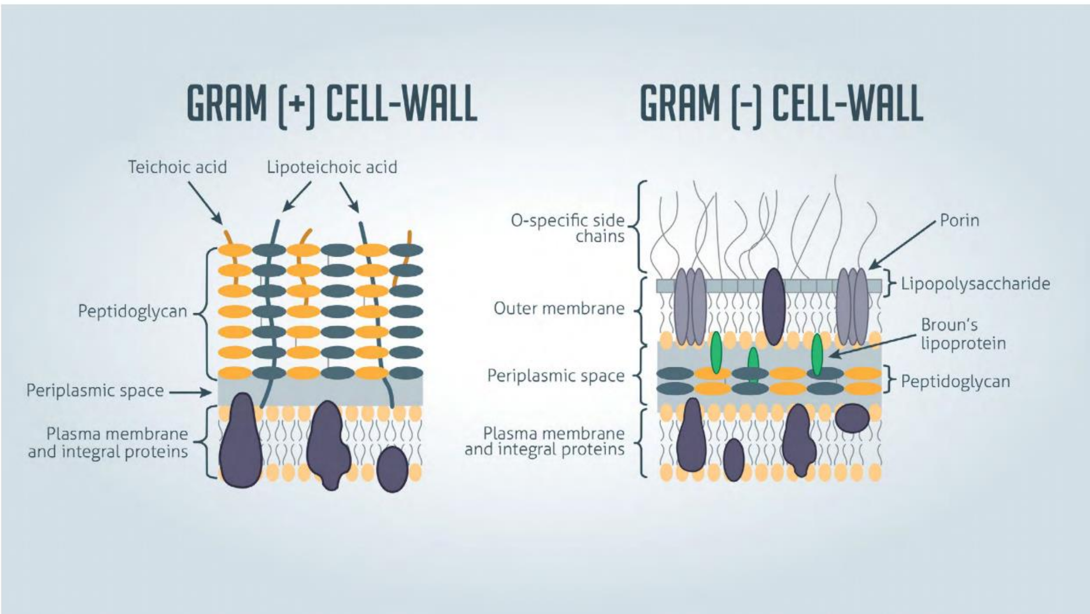

Figure 4 Schematic diagrams illustrating the difference in the bacteria cell wall composition [26]

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_2O_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_2O_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_2O-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.

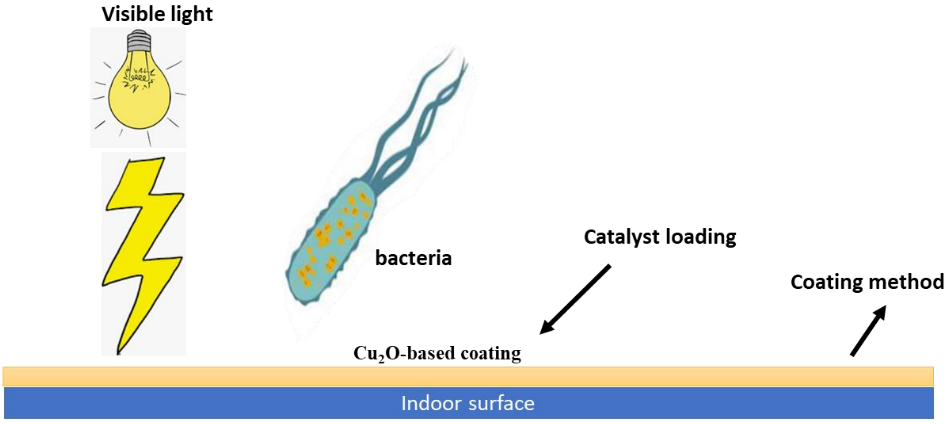

Figure 5 Parameters affecting the visible light active photocatalytic antimicrobial coating

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.

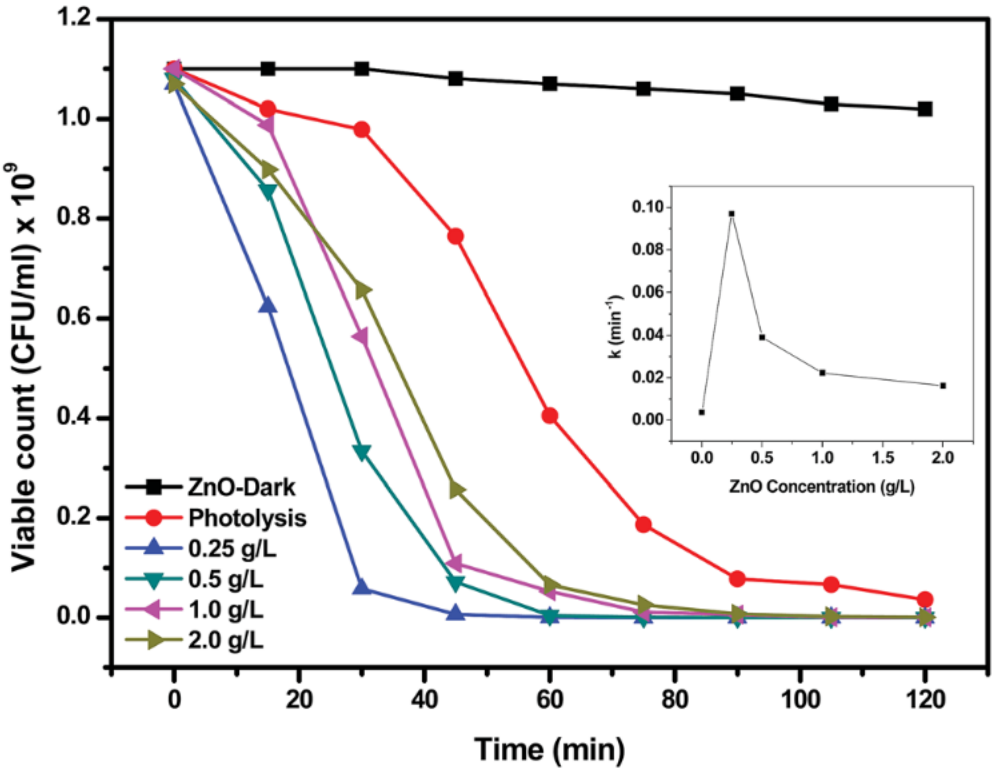

Figure 6 Effect of ZnO concentration on the inactivation of E. coli under solar light [27]

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.

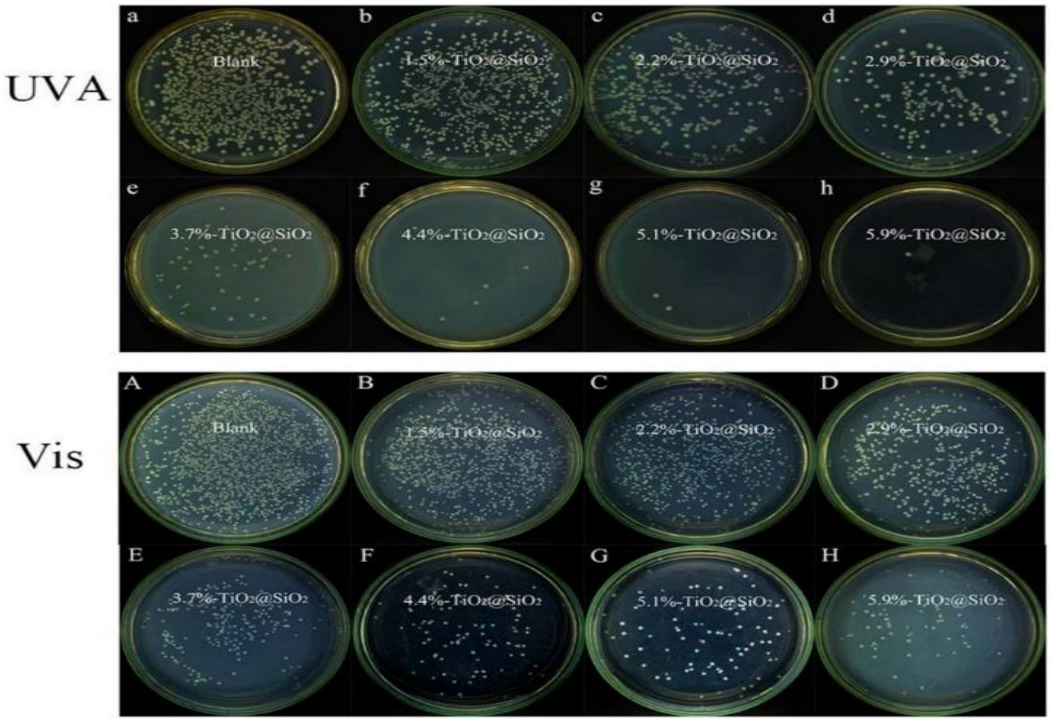

Figure 7 Antimicrobial image of the TiO2@SiO2 hybrid materials with different TiO2 contents on E. coli :(a–h) UVA irradiation and (A–H) visible-light irradiation [1]

[28] developed Fe-doped TiO_2 thin films with different doping levels on glass substrates. Figure 8 shows the surface morphology of TiO_2 thin films and 0.1% Fe-doped TiO_2 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 TiO_2 film was observed to be highly effective in inactivating *E. coli*.

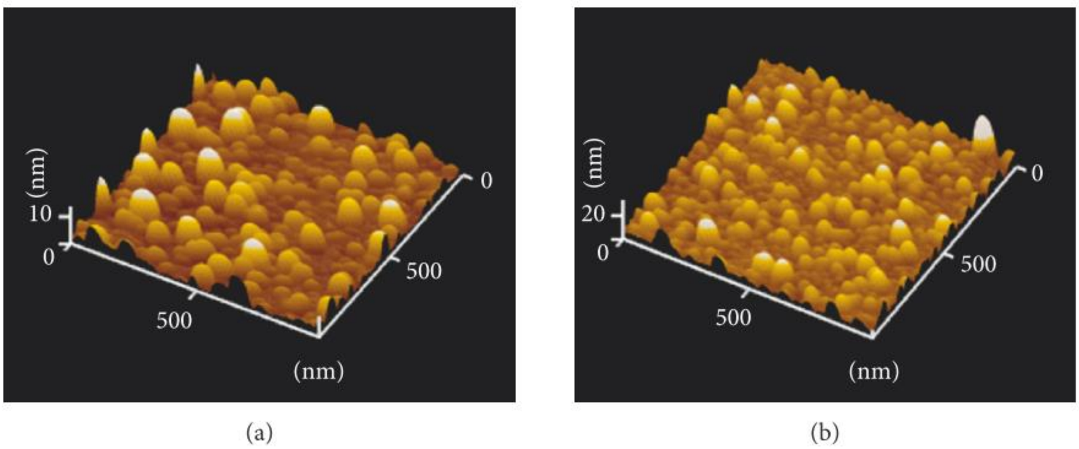

Figure 8 3D AFM images 3D AFM images of(a) bare TiO2 films and (b) 0.1 at% of Fe-doped TiO2 film [28]

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.

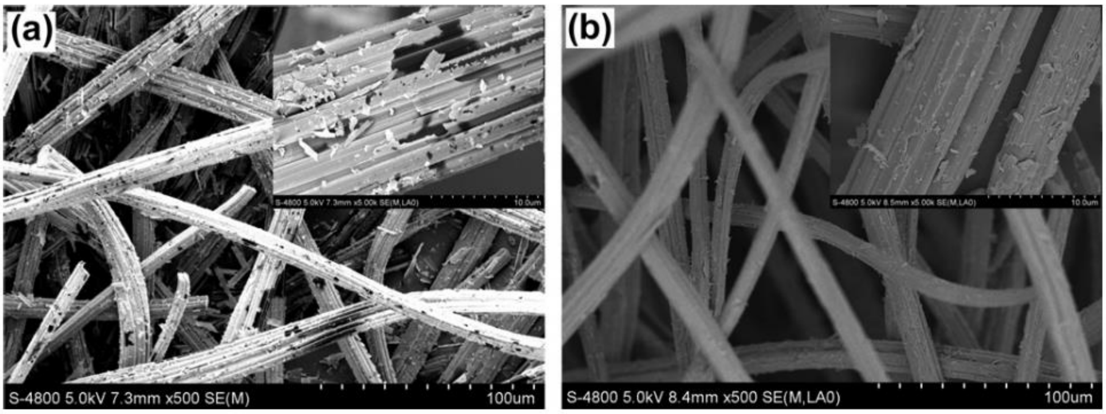

Figure 9 SEM images of samples S1-600 (a) and S2-600 (b) after ultrasonic vibration [34]

[31] 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]

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

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_2O-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_2o-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_2O-based photocatalytic antimicrobial coatings that will affect photocatalytic antimicrobial activity. Taking these factors into account, visible-light active Cu_2O-based photocatalytic antimicrobial coatings presents new opportunities and critical provisions that should be pursued for commercial uses and wide applications.

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REFERENCES

[1] Y. Chen, X. Tang, X. Gao, B. Zhang, Y. Luo, and X. Yao. 2019. Antimicrobial property and photocatalytic antibacterial mechanism of the TiO_2-doped SiO_2 hybrid materials under ultraviolet-light irradiation and visible-light irradiation. *Ceram. Int*. 45(12): 15505-15513. Doi: 10.1016/j.ceramint.2019.05.054.

[2] V. K. Yemmireddy and Y. C. Hung. 2017. Using Photocatalyst Metal Oxides as Antimicrobial Surface Coatings to Ensure Food Safety—Opportunities and Challenges. *Compr. Rev. Food Sci. Food Saf*. 16(4): 617-631. Doi: 10.1111/1541-4337.12267.

[3] C. P. Dunne *et al.* 2017. Anti-microbial Coating Innovations to Prevent Infectious Diseases (AMiCI): Cost Action ca15114. *Bioengineered*. 8(6): 679-685. Doi:10.1080/21655979.2017.1323593.

[4] J. J. Ramsden. 2015. Photocatalytic Antimicrobial Coatings. *Nanotechnol. Perceptions*. 11(3): 146-168. Doi:10.4024/n12ra15a.ntp.15.03.

[5] S. Chaturvedi and P. N. Dave. 2013. Environmental Application of Photocatalysis. *Mater. Sci. Forum*. 734(December 2012): 273-294. Doi:10.4028/www.scientific.net/MSF.734.273.

[6] V. Kumaravel *et al.* 2021 Antimicrobial TiO2 Nanocomposite Coatings for Surfaces, Dental and Orthopaedic Implants. *Chem. Eng. J.* 416(December 2020): 129071. Doi: 10.1016/j.cej.2021.129071.

[7] D. Durgalakshmi, R. Ajay Rakkesh, S. Rajendran, and M. Naushad. 2020. Principles and Mechanisms of Green Photocatalysis. January: 1-24. Doi: 10.1007/978-3-030-15608-4_1.

[8] B. A. Koiki and O. A. Arotiba. 2020. Cu2O as an Emerging Semiconductor in Photocatalytic and Photoelectrocatalytic Treatment of Water Contaminated with Organic Substances: A Review. *RSC Adv*. 10(60): 36514-36525. Doi: 10.1039/d0ra06858f.

[9] N. D. Khiavi, R. Katal, S. K. Eshkalak, S. Masudy-Panah, S. Ramakrishna, and H. Jiangyong. 2019. Visible Light Driven Heterojunction Photocatalyst of CuO-Cu_2O Thin Films for Photocatalytic Degradation of

Organic Pollutants. *Nanomaterials*. 9(7). Doi: 10.3390/nano9071011.

[10] X. Su, W. Chen, Y. Han, D. Wang, and J. Yao. 2021. In-situ Synthesis of Cu_2O on Cotton Fibers with Antibacterial Properties and Reusable Photocatalytic Degradation of Dyes. *Appl. Surf. Sci*. 56(June 2020). Doi:10.1016/j.apsusc.2020.147945.

[11] S. Luo *et al.* 2022. Mechanism Investigation for Ultra-efficient Photocatalytic Water Disinfection based on Rational Design of Indirect Z-scheme Heterojunction Black Phosphorus QDs/Cu_2O Nanoparticles. *J. Hazard. Mater.* 424(PA): 127281. Doi:10.1016/j.jhazmat.2021.127281.

[12] A. M. Nasir *et al.* 2020. A Review on Floating Nanocomposite Photocatalyst: Fabrication and Applications for Wastewater Treatment. *J. Water Process Eng*. 36(January). Doi: 10.1016/j.jwpe.2020.101300.

[13] H. Park, E. T. Bentria, S. Rtimi, A. Arredouani, H. Bensmail, and F. El-Mellouhi. 2021 Accelerating the Design of Photocatalytic Surfaces for Antimicrobial Application: Machine Learning based on a Sparse Dataset. *Catalysts*. 11(8). Doi: 10.3390/catal11081001.

[14] M. E. El-Naggar, T. A. Khattab, M. S. Abdelrahman, A. Aldalbahi, and M. R. Hatshan. 2021. Development of Antimicrobial, UV Blocked and Photocatalytic Self-cleanable Cotton Fibers Decorated with Silver Nanoparticles using Silver Carbamate and Plasma Activation. *Cellulose*. 28(2): 1105-1121. Doi: 10.1007/s10570-020-03537-4.

[15] M. M. Ibrahim *et al.* 2019. Direct Z-scheme of Cu_2O/TiO_2 Enhanced Self-cleaning, Antibacterial Activity, and UV Protection of Cotton Fiber Under Sunlight. *Appl. Surf. Sci.* 479(February): 953-962. Doi:10.1016/j.apsusc.2019.02.169.

[16] L. Valenzuela, A. Iglesias, M. Faraldos, A. Bahamonde, and R. Rosal. 2019. Antimicrobial Surfaces with Self-cleaning Properties Functionalized by Photocatalytic ZnO Electrosprayed Coatings. *J. Hazard. Mater*. 369(December 2018): 665-673. Doi:10.1016/j.jhazmat.2019.02.073.

[17] K. Kaviyarasu *et al.* 2017. Photocatalytic Performance and Antimicrobial Activities of HAp-TiO_2 Nanocomposite Thin Films by Sol-gel Method. *Surfaces and Interfaces*. 6: 247-255. Doi:10.1016/j.surfin.2016.10.002

[18] M. Ratova, J. Redfern, J. Verran, and P. J. Kelly. 2018. Highly Efficient Photocatalytic Bismuth Oxide Coatings and Their Antimicrobial Properties Under Visible Light Irradiation. *Appl. Catal. B Environ.* 239(July): 223-232. Doi:10.1016/j.apcatb.2018.08.020.

[19] Z. Du *et al.* 2018. Enhanced Photocatalytic Activity of Bi_2WO_6/TiO_2 Composite Coated Polyester Fabric Under Visible Light Irradiation. *Appl. Surf. Sci.* 435: 626-634. Doi:10.1016/j.apsusc.2017.11.136.

[20] M. Muscetta, R. Andreozzi, L. Clarizia, I. Di Somma, and R. Marotta. 2020. Hydrogen Production through Photoreforming Processes Over Cu_2O/TiO_2 Composite Materials: A Mini-Review. *Int. J. Hydrogen Energy*. 45(53): 28531-28552. Doi:10.1016/j.ijhydene.2020.07.225.

[21] A. M. Mohammed, S. S. Mohtar, F. Aziz, S. A. Mhamad, and M. Aziz. 2021. Review of Various Strategies to Boost the Photocatalytic Activity of the Cuprous Oxide-based Photocatalyst. *J. Environ. Chem. Eng*. 9(2): Doi: 10.1016/j.jece.2021.105138.

[22] Z. Yang, C. Ma, W. Wang, M. Zhang, X. Hao, and S. Chen. 2019. Fabrication of Cu_2O-Ag Nanocomposites with Enhanced Durability and Bactericidal Activity. *J. Colloid Interface Sci*. 557: 156-167. Doi: 10.1016/j.jcis.2019.09.015.

[23] P. Ganguly, C. Byrne, A. Breen, and S. C. Pillai. 2018. Antimicrobial Activity of Photocatalysts: Fundamentals, Mechanisms, Kinetics And Recent Advances. *Appl. Catal. B Environ*. 225(October 2017): 51-75. Doi:10.1016/j.apcatb.2017.11.018.

[24] I. Dincer and C. Zamfirescu. 2016. Hydrogen Production by Photonic Energy. *Sustainable Hydrogen Production*, I. Dincer and C. Zamfirescu, Eds. Elsevier. 309-391.

[25] L. Wang, C. Hu, and L. Shao. 2017. The Antimicrobial Activity of Nanoparticles: Present Situation and Prospects for the Future. *Int. J. Nanomedicine*. 12: 1227-1249. Doi: 10.2147/IJN.S121956.

[26] Karen Steward. 2019. Gram Positive vs Gram Negative. *Technol. Networks*. 1-4.

[27] S. Adhikari, A. Banerjee, N. K. R. Eswar, D. Sarkar, and G. Madras. 2015. Photocatalytic Inactivation of E. Coli by ZnO-Ag Nanoparticles Under Solar Radiation. *RSC Adv.* 5(63): 51067-51077. Doi: 10.1039/c5ra06406f.

[28] D. Meng, X. Liu, Y. Xie, Y. Du, Y. Yang, and C. Xiao. 2019. Antibacterial Activity of Visible Light-activated TiO_2 Thin Films with Low Level of Fe Doping. *Adv. Mater. Sci. Eng.* Doi: 10.1155/2019/5819805.

[29] D. Zhang, S. Lv, and Z. Luo. 2020. A Study on the Photocatalytic Degradation Performance of a [KNbO3]0.9-[BaNi0.5Nb0.5O3-: δ]0.1 Perovskite. *RSC Adv.* 10(3): 1275-1280. Doi: 10.1039/c9ra07310h.

[30] J. Hot, J. Topalov, E. Ringot, and A. Bertron. 2017. Investigation on Parameters Affecting the Effectiveness of Photocatalytic Functional Coatings to Degrade NO: TiO_2 Amount on Surface, Illumination, and Substrate Roughness. *Int. J. Photoenergy*, Doi: 10.1155/2017/6241615.

[31] I. Dundar, A. Mere, V. Mikli, M. Krunks, and I. O. Acik. 2020. Thickness Effect on Photocatalytic Activity of Tio2 Thin Films Fabricated by Ultrasonic Spray Pyrolysis. *Catalysts*. 10(9): 1-13. Doi: 10.3390/catal10091058.

[32] K. Malnieks, G. Mezinskis, and I. Pavlovska. 2017. Effect of Different Dip-coating Techniques on TiO2 Thin Film Properties. *Key Eng. Mater*. 721 (April 2017): 128-132.

Doi:10.4028/www.scientific.net/KEM.721.128.

[33] B. Fotovvati, N. Namdari, and A. Dehghanghadikolaei. 2019. On Coating Techniques for Surface Protection: A Review. *J. Manuf. Mater. Process.* 3(1). Doi: 10.3390/jmmp3010028.

[34] J. W. Shi *et al.* 2012. TiO_2/activated Carbon Fibers Photocatalyst: Effects of Coating Procedures on the Microstructure, Adhesion Property, and Photocatalytic Ability. *J. Colloid Interface Sci.* 388(1): 201-208. Doi: 10.1016/j.jcis.2012.08.038.