Photocatalytic Degradation of Pathogenic Bacteria with AgI/TiO₂ under Visible Light Irradiation

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The photocatalytic disinfection of pathogenic bacteria in water was investigated systematically with AgI/TiO₂ under visible light ($\lambda > 420$ nm) irradiation. The catalyst was found to be highly effective in killing *Escherichia coli* and *Staphylococcus aureus*. The adsorbed $\cdot\text{OH}$ and $h\nu_{\text{VB}}^+$ on the surface of the catalyst were proposed to be the main active oxygen species by study of electron spin resonance and the effect of radical scavengers. The process of destruction of the cell wall and the cell membrane was verified by TEM, potassium ion leakage, lipid peroxidation, and FT-IR measurements. Some products from photocatalytic degradation of bacteria such as aldehydes, ketones, and carboxylic acids were identified by FT-IR spectroscopy. These results suggested that the photocatalytic degradation of the cell structure caused the cell death. The electrostatic force interaction of the bacteria–catalyst significantly affected the efficiency of disinfection on the basis of the *E. coli* inactivation under different conditions.

Introduction

In 1985, Matsunaga and co-workers reported for the first time that a TiO₂ photocatalyst could kill bacterial cells in water.¹ Since then, numerous studies related to the bactericidal effect of TiO₂ photocatalysts have been reported.^{2–10} TiO₂ photocatalysts have also been applied to inactivate bacteria, viruses, and cancer cells. However, the mechanism leading to the photocatalytic killing of pathogenic microbes is still a subject of research. There are some different opinions about the bactericidal mechanisms of these photocatalysts. In the early studies, Matsunaga et al.^{1,2} proposed that the direct oxidation of coenzymes in TiO₂-treated cells, which led to the decrease in respiratory activities, was the reason for cell death. Recently, it was proposed that the destruction of the cell structure resulted in cell death. Saito and co-workers⁶ used potassium ion leakage as a criterion for measuring cell membrane damage. Kiwi and Nadtochenko⁷ found the photocatalytic degradation of lipo-polysaccharide, phosphatidylethanolcholine, and peptidoglycan, which are the main wall structure elements, at the TiO₂ interface by ATR-FT-IR. Maness et al.⁸ proposed that the loss of the membrane structure and membrane functions was the root cause of cell death when photocatalytic TiO₂ particles are outside the cell. All of these studies reported on the mechanism of TiO₂ lethality under UVA light. TiO₂ only absorbs wavelengths in the near-UV region ($\lambda < 400$ nm), which

is about 3% of the solar spectrum, and it cannot efficiently utilize visible light, which is about 43% of the solar spectrum, for photocatalytic disinfection. Therefore, visible light induced photocatalytic disinfection seems to be a promising technique from the viewpoint of using solar energy. To date, a few investigations have been conducted for photocatalytic disinfection efficiency with solar energy.^{11,12} An in-depth understanding of the mechanism is essential to devise a strategy and apply the technology in a practical system to efficiently kill a wide array of microorganisms. However, only a few studies^{13,14} have been conducted so far for visible light induced photocatalytic disinfection. Moreover, there is no direct evidence to indicate that the photocatalytic degradation of the bacterial wall membrane leads to cell death under visible light.

Recently, we have reported that the novel visible light driven photocatalyst AgI/TiO₂ shows high efficiency and photostability in the degradation of nonbiodegradable azo dyes under visible light irradiation.¹⁵ In the present study, the photocatalytic inactivation of the pathogenic bacteria *Escherichia coli* and *Staphylococcus aureus* in an aqueous AgI/TiO₂ suspension under visible light irradiation was systematically studied from the mechanistic and kinetic viewpoints. The details of photocatalytic degradation of the cell wall and the cell membrane were characterized by TEM and FT-IR measurements. The intermediates from the decomposition of bacteria were identified by FT-IR. These results verified that the degradation of the structure of the bacteria led to cell death under the visible light illuminated AgI/TiO₂ suspension.

Experimental Procedures

Materials. The reagent 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), used as the spin trapping agent in the ESR studies, was purchased from the Sigma Chemical Co. and stored at -20°C in a freezer.

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Escherichia coli (*E. coli* DH 4 α) and *Staphylococcus aureus* (*S. aureus* ATCC 6538) were purchased from the Institute of Microbiology, Chinese Academy of Sciences. All other chemicals were analytical grade. Deionized and doubly distilled water was used throughout this study.

Preparation of Photocatalysts. AgI/TiO₂ containing Ag 10 wt % was prepared by the deposition–precipitation method according to our previous report.¹⁵ A 1 g quantity of P-25 TiO₂ and 0.205 g of KI were added to 100 mL of distilled water, then 0.21 g of AgNO₃ in 2.3 mL of NH₄OH (25 wt % NH₃) was quickly added to the mixture. The resulting suspensions were stirred at room temperature for 12 h. The product was filtered, washed with water, and dried at 70 °C. Yellow AgI/TiO₂ was obtained.

Characterization. Electron spin resonance (ESR) spectra were obtained using a Bruker model ESP 300 E electron paramagnetic resonance spectrometer. A 350-W Xe arc lamp with a UV cutoff filter ($\lambda > 420$ nm) served as the irradiation light source. The settings were center field, 3480.00 G; microwave frequency, 9.79 GHz; and power, 5.05 mW. Determination of the concentration of H₂O₂ formed in the catalyst aqueous suspension under visible light irradiation was performed with a photometric method described in the literature.¹⁶ The zeta potential of catalysts in the KNO₃ (10^{−3} M) solution and bacteria cells in the NaCl (0.1 M) solution were measured with a Zetasizer 2000 (Malvern Co.). Every reading of the instrument was recorded after three consistent readings had been attained.

Bactericidal Activity. Two types of bacteria, *E. coli*, a Gram-negative bacterium, and *S. aureus*, a Gram-positive bacterium, were used as model bacteria in this study. They were incubated in Luria–Bertani (LB) nutrient solution at 37 °C for 18 h with shaking and then washed by centrifuging at 4000 rpm. The treated cells were then resuspended and diluted to $\sim 1 \times 10^8$ colony-forming units (cfu/mL) with 0.9% saline. All materials used in the experiments were autoclaved at 121 °C for 25 min to ensure sterility. The diluted cell suspension and photocatalyst were added to a 100 mL beaker with a cover. The final photocatalyst concentration was adjusted to 0.2 g/L, and the final bacterial cell concentration was $\sim 8 \times 10^7$ cfu/mL. The reaction volume was 30 mL. The reaction mixture was stirred with a magnetic stirrer throughout the experiment. The light source for photocatalysis was a 350-W Xe arc lamp (Shanghai Photoelectronic Devices, Ltd.). Light was passed through a water filter and a UV cutoff filter ($\lambda > 420$ nm) and then was focused onto the beaker reactor. The intensity of the illumination was 2.8 mW/cm². The reaction temperature was maintained at 25 °C. The initial solution pH was adjusted by aqueous solutions of NaOH or HCl, and the solution pH varied less than one pH unit throughout the reaction. A bacterial suspension without photocatalyst was irradiated as a control, and a reaction mixture with no visible light irradiation was used as a dark control. Before and during the light irradiation, an aliquot of the reaction solution was immediately diluted with saline, and an appropriate dilution of the sample was incubated at 37 °C for 24 h on nutrient agar medium, and then the colonies were counted to determine the number of viable cells. Samples for FT-IR analysis were prepared by the following procedure. The suspensions at different irradiation times were evaporated by a freeze-drying method. For FT-IR measurement, the dry residue was supported on KBr pellets. The infrared spectrum was recorded on a Nicolet FT-IR spectrophotometer. For the measurement of K⁺ leakage from the inactive bacteria, at every time interval, 1 mL of the illuminated bacterial suspension was centrifuged, and the supernatant was used for inductively coupled plasma optical emission spectrometry (ICP-OES, OPTIMA 2000, Perkin-Elmer, Inc.). All the previous experiments were repeated 3 times.

Determination of Lipid Peroxidation. Formation of malondialdehyde (MDA) was used as an index to measure lipid peroxidation. MDA was quantified based on its reaction with thiobarbituric acid (TBA) to form a pink MDA-TBA adduct.¹⁷ A quantity (10⁸ cfu/mL) of cells was mixed with 0.2 g/L AgI/TiO₂, and the suspension was irradiated. At given time intervals, 1 mL of the illuminated bacterial

Figure 1. Temporal course of the *E. coli* inactivation ($\sim 5 \times 10^7$ cfu/mL, 30 mL, pH = 4.04) in aqueous dispersions containing 0.2 g/L catalysts under visible light irradiation. (a) No catalyst, (b) TiO₂, (c) AgI/TiO₂ in the dark, and (d) AgI/TiO₂.

suspension was mixed with 2 mL of 10% (wt/vol) trichloroacetic acid, and the solids were removed by centrifugation at 7000–8000 rpm. A total of 3 mL of freshly prepared 0.67% (wt/vol) TBA (Sigma Chemical Co.) solution was then added to the resulting supernatant. The samples were incubated in a boiling water bath for 10 min and cooled, and the absorbance at 532 nm was measured with a 752N spectrophotometer (Shanghai Precision and Scientific Instrument Co., Ltd.). The concentrations of the MDA formed were calculated based on a standard curve for the MDA (Sigma Chemical Co.) complex with TBA; the E_{532} was 49.5 mM^{−1} cm^{−1}. All the previous experiments were repeated 3 times.

Transmission Electron Microscopy (TEM). A quantity (10⁸ cfu/mL) of cells was mixed with 1.6 g/L AgI/TiO₂, and the suspension was irradiated. At given time intervals, the cell suspensions were collected and centrifuged down to pellets. For the TEM analysis of *E. coli*, all samples were prepared according to the following standard procedures.¹⁸ The bacteria pellets were pre-fixed in 2.5% glutaraldehyde at 4 °C for 12 h and then washed 2 times with 0.1 M phosphate buffer (PBS) (pH 7.2). After the specimens had been washed with PBS, they were rendered by mixing with 2% Na₂H₂P(W₂O₇)₆ aqueous solution at a volume ratio of 1:1 for 2 h. Then, the mixing suspensions were dropped onto copper grids with a holey carbon film. The grids were dried under natural conditions and examined using a TEM Hitachi H-7500. The same experiments were repeated 3 times.

Results and Discussion

Bacterial Inactivation under Visible Light Irradiation. The bactericidal activities of the samples were evaluated by the inactivation of *E. coli* in water under visible light irradiation. As shown in Figure 1, 7.8 log *E. coli* was almost completely killed within 60 min in the AgI/TiO₂ suspension under visible light irradiation (Figure 1, curve d). However, in the dark, AgI/TiO₂ did not show any bactericidal effects on *E. coli* (Figure 1, curve c), indicating that the photocatalyst itself is not toxic to *E. coli*. Neither visible light nor the combination of TiO₂ and visible light showed any activity for the killing of *E. coli* (Figure 1, curves a and b). The diffuse reflectance UV–vis spectra of AgI/TiO₂ exhibited a visible light absorption band around 400–436 nm (Figure S1, Supporting Information), and the absorption peak around 425 nm was assigned to the direct band gap.¹⁹ These results indicated that AgI was the active component of the catalyst under visible light irradiation. The effects of cell concentrations on the inactivation of *E. coli* were performed in visible light illuminated AgI/TiO₂ (Figure S2, Supporting Information). The concentration of 4.7×10^6 cfu/mL of *E. coli* was completely inactivated within 15 min, while 6.9×10^7 cfu/mL was completely killed at 60 min of irradiation. With the initial concentration

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Figure 2. DMPO spin trapping ESR spectra recorded at ambient temperature in aqueous AgI/TiO₂ dispersion under visible irradiation ($\lambda > 420$ nm).

Figure 3. Inactivation of *E. coli* ($\sim 5 \times 10^7$ cfu/mL) under different pH conditions with visible light illuminated AgI/TiO₂.

increasing, the inactivation rate decreased. However, the initial concentration of 1.2×10^9 cfu/mL was also completely removed at 120 min of irradiation. These results indicated that the catalyst was highly effective at the killing of *E. coli* under visible light. To illustrate the AgI/TiO₂ visible light induced bactericidal mechanism, the ESR spin trap technique (with DMPO) was used to detect the nature of the reactive oxygen species generated on the surface of the catalyst under visible light irradiation. A 350-W Xe arc lamp with a UV cutoff filter ($\lambda > 420$ nm) was employed to irradiate the aqueous suspension catalyst samples. Four characteristic peaks of DMPO- $\cdot$ OH were observed in the AgI/TiO₂ suspension (Figure 2).²⁰ No such signals were detected in the sample without irradiation. This means that irradiation was essential for the generation of $\cdot$ OH on the surface of the catalyst. In the ESR experiments, no $\text{O}_2^{\cdot-}$ radicals were detected in AgI/TiO₂ dispersions in methanolic media under otherwise identical conditions.²¹ Furthermore, in the visible light irradiated AgI/TiO₂ system, the formation of H₂O₂ also was detected as shown in the previous work.¹⁵ The results indicated that $\cdot$ OH and H₂O₂ reactive species were involved in the photocatalytic bactericidal reaction. *S. aureus* was also killed efficiently in aqueous AgI/TiO₂ suspensions under visible light irradiation. The 7 log *S. aureus* inactivation occurred after 100 min of irradiation.

Interaction of Bacteria-AgI/TiO₂. The effect of pH on photocatalytic inactivation of bacteria was investigated. As shown in Figure 3, at pH = 4.04, the inactivation of *E. coli* was the highest; 6.1 log *E. coli* inactivation occurred at 40 min irradiation, while at pH = 7.75, only 0.67 log *E. coli* inactivation was observed at the same irradiation time. The results indicated that the pH had a great influence on the *E. coli* inactivation. The charges of the bacteria and AgI/TiO₂ under different pH conditions are shown in Figure 4. In the range of pH 2–9, the overall charges of *E. coli* were negative, while the surface charge property of

Figure 4. Zeta potentials for a suspension of 1.0 g/L AgI/TiO₂ in the presence of KNO₃ (10^{-3} M).

Figure 5. Survival of *E. coli* with visible light illuminated AgI/TiO₂ dispersions (0.2 g/L, pH = 7) under otherwise different conditions: (a) Ni(NO₃)₂ with no catalyst, (b) Mg(NO₃)₂ with no catalyst, (c) without the addition of cation, (d) Mg(NO₃)₂, and (e) Ni(NO₃)₂. Cation concentration: 30 μ M.

AgI/TiO₂ changed with the change of solution pH. The isoelectric point of AgI/TiO₂ was about 5.1. At pH < 5.1, the surface of the catalyst was positively charged, while it was negatively charged at pH > 5.1. Therefore, at pH = 4.04, electrostatic attraction existed between *E. coli* and catalyst, leading to *E. coli* being tightly bound with the catalyst surface. Thus, a higher inactivation rate was obtained. At pH > 5.1, the electrostatic repulsive force between the *E. coli* and the catalyst increased with the pH increasing due to the more negative zeta potential. This led to the reduction of the *E. coli* inactivation rate. The zeta potential of *E. coli* tended to be less negative at pH = 6.03. Thus, the inactivation of *E. coli* was inhibited to some extent. However, a stronger electrostatic repulsive force resulted in lower bactericidal efficiency at pH = 7.75. At pH = 8.78, the zeta potentials of the catalyst and *E. coli* did not change much as compared with the condition of pH = 7.75, so the inactivation rate of *E. coli* was similar to that at pH = 7.75. These results were attributed to the interaction of bacteria and AgI/TiO₂. Hamouda and Baker²² also showed that if the antimicrobial composition had the same charge as the bacteria cells, this induced repulsion and prevented contact, while the addition of EDTA/Tris buffer to the formulation changed the charge and considerably improved the activity of the formulation. To further study the effects of the interaction between bacteria and catalyst, Ni²⁺ or Mg²⁺ was added into the reaction system. As shown in Figure 5, the *E. coli* inactivation rate was greatly increased with the addition of Ni²⁺ or Mg²⁺ at pH = 7.75. The 7.5 log *E. coli* was completely killed under 60 min irradiation in the presence of 30 μ M Ni²⁺, and 7 log *E. coli* inactivation occurred at 60 min irradiation in the presence of 30 μ M Mg²⁺. The single 30 μ M Ni²⁺ or Mg²⁺ did not show any bactericidal effect (Figure 5, curves a and b), indicating that the tested concentration of inorganic ions did not inhibit the growth of bacteria. Furthermore, the zeta potential measurement (Figure 6) showed that the zeta potential of AgI/TiO₂ was more positive in the presence of Ni²⁺

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Figure 6. Zeta potentials for different suspensions of 1.0 g/L AgI/TiO₂ in the presence of KNO₃ (10⁻³ M): (a) 30 μM Ni (NO₃)₂, (b) 30 μM Mg (NO₃)₂, and (c) without the addition of ions.

or Mg²⁺ than without the addition of ions. A weaker repulsive electrostatic force occurred between catalyst and bacteria at pH = 7.5, resulting in higher bactericidal activity. The zeta potential of the catalyst became more positive with the addition of Ni²⁺ than with the addition of Mg²⁺, resulting in a greater inactivation rate in the presence of Ni²⁺ than in the presence of Mg²⁺. This result further confirmed the role of interaction for *E. coli*-AgI/TiO₂ in disinfection, although the addition of Ni²⁺ or Mg²⁺ may enhance the separation of photogenerated electrons and holes. All of the previous experimental results indicated that the electrostatic force interaction of the bacteria and catalyst is crucial for high bactericidal efficiency. Additional examinations of the effects of methanol and inorganic anions HCO₃⁻, SO₄²⁻, and H₂PO₄⁻ on the inactivation rate of *E. coli* also were performed (Figure S3, Supporting Information). Methanol alone showed hardly any bactericidal effects on *E. coli* under visible light irradiation (Figure S3, curve a), indicating that methanol itself at the tested concentration is not toxic to *E. coli*. When methanol was introduced into the photoreaction system of AgI/TiO₂, the rate of *E. coli* inactivation slowed down to some extent (Figure S3, curve e). Methanol has been found to both scavenge holes and react with •OH.²³ Since methanol does not strongly adsorb on TiO₂ in aqueous systems,^{24,25} the interaction of electrostatic forces between *E. coli* and catalyst was not changed by the addition of methanol. It predominantly scavenged the free •OH radicals in the solution and did not affect the role of the adsorbed •OH (•OH_{ad}) and holes (h_{VB}⁺) on the surface of the catalyst. The result indicated that •OH_{ad} and h_{VB}⁺ were possible reactive species for the inactivation of *E. coli*. Furthermore, the addition of HCO₃⁻, SO₄²⁻, and H₂PO₄⁻ ions led to a marked suppression in the rate of *E. coli* inactivation (Figure S3, curves b–d). These ions might play two roles in the photocatalytic inactivation of *E. coli*. The first one was that their high adsorption on the surface of TiO₂²⁶ caused the formation of a negatively charged layer on the surface of the catalyst, which repulsed bacteria, resulting in a slower disinfection rate. Another was that these adsorbed ions reacted with •OH_{ad} and h_{VB}⁺ to form HCO₃•⁻, SO₄•⁻, and H₂PO₄•⁻, which are less reactive than •OH_{ad} and h_{VB}⁺.

Destruction of Cell Structure Checked by TEM and K⁺ Leakage. To understand the bactericidal mechanism of various reactive species (e.g., •OH, O₂•⁻, and H₂O₂), the morphology of bacteria at different stages during bactericidal experiments was investigated by TEM. Figure 7A shows the TEM images of *E. coli*. The characteristics of the bacteria are a well-defined cell wall as well as the evenly rendered interior of the cell, which corresponds to the presence of proteins and DNA. Great changes had taken place to the morphology of *E. coli* that had been

illuminated for 30 min (Figure 7B). The cell wall was decomposed, and the rendered interior of the cell became white, indicating that the outer membrane of the cell was damaged, leading to a leakage of the interior component. This phenomenon was more significantly shown in the images of *E. coli* with 2 h irradiation (Figure 7C,D). With irradiation time increasing, the catalyst nanoparticles penetrated inside the cells, resulting in more damage to the membranes of the cells. The lipopolysaccharide layer of the outer membrane plays an essential role in providing a barrier of selective permeability for *E. coli* Gram-negative bacteria. On the basis of the TEM investigation, the AgI/TiO₂ photocatalyst could decompose the cell wall and the cell membrane by reactive species, leading to a change in the cell membrane permeability and a resultant leakage of intracellular substances. K⁺ exists universally in bacteria⁶ and plays a role in the regulation of polysome content and protein synthesis. Therefore, K⁺ leakage from the inactivated bacteria was used in this work to examine the permeability of the cell membrane (Figure 8). In both AgI/TiO₂ in the dark and with only visible light irradiation (control experiments), there was nearly the same K⁺ leakage from *E. coli* cells. The K⁺ concentration gradually increased and became approximately steady with increasing reaction time. In the visible light illuminated AgI/TiO₂ suspensions, K⁺ immediately leaked out, and the leakage increased in parallel with the inactivation of *E. coli* with irradiation time, and the total K⁺ content (2.66 ppm) from the tested *E. coli* was completely released when all the *E. coli* was completely killed at 60 min of irradiation. This result suggested that the cell membrane permeability had been disrupted with the inactivation of *E. coli*.

Lipid Peroxidation. As reported before, MDA is a lipidperoxidation product formed from the oxidation of *E. coli* membrane phosphatidylethanolamine.⁸ To estimate membrane damage, the formation of MDA was examined in AgI/TiO₂ suspensions under different conditions. As shown in Figure 9, when no AgI/TiO₂ was present, control cells with visible light irradiation and in the dark produced comparable low levels of MDA (Figure 9, curves c and d), indicating that the amount of preexisting MDA was negligible and that visible light alone did not result in a significant level of lipid peroxidation. Moreover, when the catalyst was in the dark, the maximum MDA (0.06 μM) was detected at an *E. coli* concentration of 3.1 × 10⁸ cfu/mL (Figure 9, curve b). Conversely, in the visible light irradiated AgI/TiO₂ suspension, the MDA concentration increased with irradiation time and reached a maximum of 0.19 μM at an *E. coli* concentration of 3.1 × 10⁸ cfu/mL (Figure 9, curve a). Subsequently, the MDA concentration decreased with irradiation time. On the basis of all the previous experiments, it is confirmed that MDA was formed and then degraded only in a visible light irradiated AgI/TiO₂ system, indicating that the peroxidation reaction of an unsaturated lipid unit of the *E. coli* membrane was first caused by the reactive active species generated from the system, to yield hydroperoxide and dialkyl-peroxides.²⁷ Furthermore, the breakdown of hydroperoxides and lipid endoperoxide radicals leads to the formation of various products including MDA.^{8,28} Continuously, MDA was further oxidized by reactive species. The results also indicated the process of the photodegradation of the cell membrane.

FT-IR Spectra of *E. coli* Treated with AgI/TiO₂ under Visible Light Irradiation. Figure 10 shows the FT-IR spectra of *E. coli* as a function of time during AgI/TiO₂ visible light photocatalysis. In the FT-IR spectra of *E. coli*, the specific

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Figure 7. TEM images of *E. coli* for different reaction times in visible light illuminated AgI/TiO₂ suspension: (A) *E. coli* before reaction, (B) *E. coli* treated for 30 min, and (C and D) *E. coli* treated for 120 min.

Figure 8. Leakage of K⁺ from *E. coli* cells under different conditions: (a and b) AgI/TiO₂ dispersions (0.2 g/L) with and without visible light and (c) visible light with no catalyst.

Figure 9. Concentration of MDA from lipid peroxidation of *E. coli* changes with reaction time under different conditions: (a and b) AgI/TiO₂ dispersions (0.2 g/L) with and without visible light and (c and d) with and without visible light in the absence of AgI/TiO₂.

functional groups were obtained by referencing the reported values for biomolecules and bacteria cells.²⁹ In Figure 10A, the characteristic peaks at 3295 and 3062 cm⁻¹ were assigned to

Figure 10. Changes of FT-IR spectra of *E. coli* during the photocatalytic inactivation of *E. coli*. (A) Bands in the spectral region of 4000–2500 cm⁻¹ and (B) bands in the spectral region of 1900–900 cm⁻¹.

amide A and amide B, respectively, while the peaks at 2963, 2927, 2852, and 2872 cm⁻¹ were attributed to ν_a (CH₃), ν_a (CH₂), ν_s (CH₃), and ν_s (CH₂), respectively. With irradiation time increasing, these characteristic peaks decreased. After 6 h, amide A at 3295 cm⁻¹ and amide B at 3062 cm⁻¹ disappeared, and also the peak intensity of the C–H bands at 2872 and 2852 cm⁻¹ disappeared. The two peaks at 2963 and 2927 cm⁻¹ were almost undetectable. Concomitantly, the wide band of the OH⁻ vibrations in the skewed form with a maximum at around 3347 cm⁻¹. Figure 10B shows significant changes of

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the initial band shapes of the oligosaccharide bands around 1087 cm^{-1} , and profile changes of the PO_2^- band near 1242 cm^{-1} , as well as the decay of the amide I band near 1653 cm^{-1} and the amide II band near 1545 cm^{-1} . In parallel, an increase in absorbance in the region related to the $\text{C}=\text{O}$ bonds of aldehydes and ketones between 1690 and 1734 cm^{-1} was observed. After 120 min, the most prominent peaks were seen at 1408 and 1337 cm^{-1} , indicating an increase in the concentration of carboxylic groups. The results revealed that the formation of carboxylic acid occurred with the photocatalytic degradation of the cell membrane. Similarly, the spectral profiles of the FT-IR spectra of *S. aureus* with irradiation time also showed almost the same changes as *E. coli* during AgI/TiO₂ photocatalysis under visible light irradiation (Figure S4, Supporting Information). Some initial spectral profile of *S. aureus* disappeared or decayed with increasing irradiation time. Equally, the carboxylic groups' peak at 1337 cm^{-1} appeared after 120 min (Figure S4B, Supporting information) and increased with increasing irradiation time, indicating the formation of carboxylic acid. The results indicated that the cell wall and membrane were degraded by the oxidation of the reactive species, resulting in cell death.

Conclusion

AgI/TiO₂ is highly effective for the killing of pathogenic bacteria under visible light irradiation. The destruction of *E. coli*

and *S. aureus* cells was followed by TEM, FT-IR, and the formation and degradation of MDA. By FT-IR measurement, it was found that the constituents of the cell wall membranes disappeared and that some intermediates such as aldehydes, ketones, and carboxylic acids were formed. The results provide solid evidence for the photocatalytic degradation of pathogenic bacteria under visible light irradiation. According to the results of electron spin resonance and the effect of radical scavengers, H_2O_2 , free $\cdot\text{OH}$, adsorbed $\cdot\text{OH}$, and h_{VB}^+ on the surface of the catalyst, reactive active oxygen species were involved in the photocatalytic reaction. The bactericidal activity obtained under various experimental conditions indicated that the electrostatic force interaction of the bacteria with the catalyst is crucial for high bactericidal efficiency.

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Supporting Information Available: Results for the UV-vis diffuse reflectance spectra of AgI/TiO₂, effects of different *E. coli* initial concentrations, effect of methanol and inorganic anions, and FT-IR of *S. aureus* treated for different times. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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