Application of high specific surface area Ag/AgCl/TiO₂ coupled photocatalyst fabricated by fused filament fabrication

Zheng-Rong Yang¹ · Po-Ching Lee² · Chun-Yu Kuo¹ · Chung-Hao Shin¹ · Ching-Bin Lin¹

Received: 17 January 2022 / Accepted: 7 March 2022 / Published online: 17 March 2022
© The Author(s), under exclusive licence to Springer-Verlag London Ltd., part of Springer Nature 2022

Abstract
This study used a three-dimensional (3D) printing process to develop the Ag/AgCl/TiO₂ coupled photocatalyst with a specific surface area of 748 mm²/g. We examined the catalytic capability of this photocatalyst in degrading methyl blue (MB) dye and sterilizing Escherichia coli as well as the durability and reliability of its continuous use. A TiO₂ module was constructed through fused filament fabrication (FFF), and the adopted 3D printing filament was composed of anatase TiO₂ nanoparticles, stearic acid, wax, and a plasticizer. The green compact of the TiO₂ module was subjected to solvent debinding, thermal debinding, and sintering to obtain a fundamental structure that was subsequently coupled with AgCl through a precipitation reaction. Ultraviolet radiation was used for the photoreduction to obtain the Ag/AgCl/TiO₂ coupled photocatalyst coupling module. This photocatalyst can effectively degrade MB dye and disinfect E. coli. The degradation of MB dye and sterilization of E. coli were conducted under visible and ultraviolet light. The degradation of MB dye by the Ag/AgCl/TiO₂ coupled photocatalyst was a first-order reaction. In addition, this coupled photocatalyst could retain its MB dye degradation rate (95%) for five cycles. E. coli was sterilized using the prepared photocatalytic module in a 120-min test, and this sterilization phenomenon could be presented as a hyperbolic reaction. The photocatalytic module manufactured in this study through FFF could efficiently degrade pollutants in water, and its durability and reliability after repeated use have been approved.

Keywords Silver chloride · Fused filament fabrication · Methyl blue dye · Escherichia coli · Reliability

1 Introduction
The textile dyeing and finishing industry discharges a large quantity of industrial waste that contains numerous chemically toxic pigments and dyes into bodies of water, which results in their pollution and causes serious harm to humans and the natural environment [1]. Traditional industrial wastewater treatment methods include coagulation and biological treatment; however, industrial wastewater treated using these methods does not meet discharge standards. Traditional drinking water disinfection usually involves chlorination procedures. Chlorination is the addition of chlorine or chlorine byproducts to drinking water for disinfection. Although this method has a strong disinfection effect, chlorinated drinking water frequently has a peculiar smell and may even contain some potentially toxic or mutagenic products, such as trihalomethane and chloroform, which are often carcinogenic. Photocatalysis technology enables the nontoxic, nonpolluting, and efficient treatment of dyes in industrial wastewater and the sterilization of drinking water [2]. For example, anatase TiO₂ nanoparticles can generate electron–hole pairs after absorbing a certain wavelength of photon energy. Holes interact with water molecules to form (OH) free radicals with a strong oxidizing ability. Electrons and oxygen combine to produce (O₂⁻) free radicals. These free radicals can degrade dyes and disinfect bacteria. Anatase TiO₂ nanoparticles are widely used photocatalysts with high photocatalytic efficiency and photocatalytic activity [3]. However, because the energy gap of anatase TiO₂ is approximately 3.2 eV, this photocatalyst is only suitable for use with ultraviolet light with a wavelength of less than 380 nm and is rarely used with sunlight. The ultraviolet light absorption band covers only 5% of the solar spectrum; thus,
the applicability of anatase TiO₂ nanoparticles as a catalyst is limited [4]. Consequently, some studies have developed new photocatalyst materials for utilization under sunlight. For example, the AgX (X = Cl, Br) photocatalyst forms silver radicals after being irradiated. Because of the surface plasmon resonance effect of silver clusters, the AgX photocatalyst exhibits excellent photocatalytic activity under visible light [5]. According to Kakuta et al. [6], Ag (silver clusters)/AgCl, which can absorb visible light, has a stronger photocatalytic effect than does nitrogen-doped TiO₂. Ag/AgCl almost eliminates the proliferation ability of bacteria in a short time and causes cell death. In addition, to achieve effective photocatalysis under visible light, photocatalysts containing AgCl and metal or nonmetal oxides, such as Ag/AgCl/WO₃ [7], Ag/AgCl/MCM-41 [8], Ag/AgCl/TiO₂ [9], Ag/AgI/Al₂O₃ [10], Ag/AgCl/ZnO [11], and Ag/AgCl/rGO [12], Ag/AgCl/SiO₂/GO [13], Ag/AgCl-NC [14], Ag/AgCl/MIL-88A(Fe) [15], Ag/AgCl/Tubular g-C₃N₄ [16], Ag/AgCl/BiO₂-x [17], and Ag/AgCl/Bi₂O₃/BiFeO₃ [18] have been developed. Some studies have indicated that the combination of TiO₂ with Ag/AgCl can strengthen the catalytic effect of visible light and increase the stability of degradation [19–23]. Yang et al. [9] synthesized the Ag/AgCl/TiO₂ coupled photocatalyst by using the sol–gel method and the hydrothermal method combined with the ion exchange method, and degraded Rose Bengal under xenon lamp irradiation. The Ag/AgCl/TiO₂ coupled photocatalyst is superior to TiO₂ and Ag/TiO₂ because it has a lower recombination rate of electrons and holes.

Zhang et al. [19] synthesized the Ag/AgCl/TiO₂ coupled photocatalyst by using a solvothermal method. Under visible light irradiation, this photocatalyst exhibits high photocatalytic activity and can quickly sterilize Escherichia coli. This phenomenon occurs because after Ag/AgCl is coupled with TiO₂, the recombination rate of electrons and holes decreases, and the minority carrier separation rate increases during the photocatalytic reaction, as indicated by steady-state and transient photoluminescence spectra. According to Shah et al. [21], when Ag/AgCl/TiO₂ is used for the photocatalytic degradation of methyl orange under visible light, CuO can be mixed into the methyl orange solution as an additional catalyst (catalysis occurs through electron absorption). According to Guo et al. [7], Ag/AgCl/TiO₂ coupled photocatalysts prepared through the deposition–precipitation method and photoreduction method have high photocatalytic activity and can effectively degrade 4-chlorophenol and hexavalent chromium ions under visible light irradiation. The high photocatalytic activity of these photocatalysts is attributed to the surface plasmon resonance effect of silver clusters. According to Guan et al. [24], when the Ag/AgCl/ZIF-8/TiO₂ photocatalyst coating cotton fabric is used, the photocatalytic degradation of methylene blue (MB) solution can reach 98.5% in 105 min under visible light irradiation.

The kinetic constant of this first-order photocatalytic degradation is 0.0332 min⁻¹. In addition, this photocatalyst can maintain a degradation rate of approximately 85% after three degradation cycles. However, although a particle suspension of a Ag/AgX (X = Cl, Br)/TiO₂ coupled photocatalyst has high photocatalytic efficiency, it has several drawbacks. First, the Ag/AgCl/TiO₂ coupled photocatalyst is used to degrade dyes, it must be subjected to complicated filtration and centrifugal separation before being reused, which limits its practical applicability. Second, if Ag/AgCl/TiO₂ coupled photocatalyst particles cannot be recycled effectively, they flow into water sources and land, thereby causing secondary pollution. According to Nakhostin Panahi et al. [25], the Ag/AgCl/TiO₂ nanocomposite is capable of removing volatile organic pollutants (VOCs) under the irradiation of visible and UV light. According to Bao et al. [26], in the photocatalytic degradation of reactive red X-3B, Ag/AgCl/TiO₂ continuous fibers exhibited significantly enhanced activities under separate visible or UV light irradiation, in comparison to TiO₂ fibers. According to Yang et al. [27], Ag/AgCl/TiO₂/PM ( hierarchical porous magnesian) material has a higher visible and ultraviolet light absorption response and excellent gas absorption performance compared to other controls. Its photocatalytic reaction rate was 5.21 and 30.57 times higher than that of TiO₂/PM and TiO₂/imporous magnesian substrate. According to Ghasemi et al. [28], they synthesized the Ag/AgCl@TiO₂ plasmonic photocatalyst with enhanced photoactivity under sunlight by a facile biosynthesis method. A topmost eosin Y dye photodegradation of 99% was attained at pH 4 with the photocatalyst concentration of 0.05 g/100 mL and the eosin Y concentration of 50 mg/L at the ambient temperature.

Some ceramic three-dimensional (3D) printing technologies, such as fused filament fabrication (FFF), ceramic extrusion deposition, binder jet deposition, powder sintering deposition, paste extrusion deposition, selective laser sintering, direct ceramic inkjet, and photopolymerization, have been developed to manufacture 3D ceramic structures. FFF can be used to create nanocomposites and ceramic structures [29–35]. According to Vidakis et al. [29], PP/TiO₂ nanoparticle composite filaments and their nanocomposites were fabricated using a melt-mixing extrusion and FFF process, respectively. The performance of the nanocomposite increases with the amount of TiO₂ filler, while the microstructural effects and processing properties of the material are not significant. According to Brounstein et al. [32], PLA/antimicrobial ceramics (ZnO and TiO₂) composite filaments exhibit thermal phase behaviors and thermal stability suitable for 3D printing, and a poly (ethylene glycol) plasticizer can be used to tune the mechanical properties without affecting the antimicrobial efficacy that ZnO and TiO₂ imbue. According to Vidakis et al. [33], they used acrylonitrile butadiene styrene (ATO, TiO₂) nanocomposite filaments.
and the FFF process to make three-dimensional printed structures. Appropriate ATO, TiO₂ nanofiller content can increase the mechanical properties of 3D structures. According to Sangiorgi et al. [34], titanium oxide–based photocatalytic filters were produced by fused deposition modelling; PLA/30 wt% TiO₂ nanoparticle photocatalyst exhibits 100% methyl orange (MO) degradation after 24 h of light exposure. According to Sevastaki et al. [35], 100% recycled solid polystyrene composed with 40% w/w TiO₂ nanoparticles to make composites filaments, which are then printed using the FDM process to make 3D structures with photocatalytic effects. The manufacturing process of a ceramic fused filament fabrication involves feeding a continuous filament into a heated nozzle and then melting, extruding, depositing, and printing this molten filament on the printing tablet. The continuous filament used in ceramic FFF is a thermoplastic material that contains ceramic particles; short fibers; or other ingredients, such as wax and stearic acid. After the 3D printing of a green embryo, the embryo is moved into solvent or heating degreasing equipment to remove the thermoplastic and organic components and then sintered to densify the printed workpiece to form a block structure.

In the present study, fused filament fabrication was used to manufacture a 3D-printed module of Ag/AgCl/TiO₂ coupled photocatalyst. This module was used for the degredation of the methyl blue (MB) dye and the sterilization of environmental Escherichia coli (E. coli). Moreover, the durability and reuse reliability of the Ag/AgCl/TiO₂ coupled photocatalyst module were tested.

2 Experimental

2.1 Fabrication of 3D printing wire

In FFF, a continuous filament is used to print 3D objects, and a continuous 3D printing wire is manufactured using an extrusion molding machine. The 3D printing wire fabricated in this study comprised anatase powder (50%) with 20-nm particles, high-density polyethylene (40%), wax (4.5%), stearic acid (1.5%), and a plasticizer (4%).

These materials were stirred in a Banbury mixer (Well Shyang Machinery Co., LTD., SBI-3L, R.O.C.) at 50 rpm and 175 °C for 30 min to ensure that all the ingredients were completely melted and mixed evenly. The obtained mixture was then cut into pellets, fed into a single-screw extruder (Der-Hsin Plastic Machinery, R.O.C), and extruded to form linear filaments. The barrel temperatures from zones 1 to 4 were 160 °C, 180 °C, 180 °C, and 160 °C, respectively. The screw speed was 30 rpm, and the take-up rate was 2.3 m/min. The round extruder dies with diameters of 1.75 mm, and the diameter of the filament after extrusion was 1.70–1.80 mm, and the ovality of the filament was 0.1 mm (an ovality of 0 represents a true circle).

2.2 Ceramic fused thread of 3D printing head, module design, and manufacturing

The fabricated Ag/AgCl/TiO₂ coupled photocatalyst module comprised the Ag/AgCl/TiO₂ coupled photocatalyst cylinder with a specific surface area of 748 mm²/g, a stirring shaft, and polyactic acid (PLA) upper and lower pressing plates. The central circular hole of the PLA pressing plate contained internal threads that could be connected to the external threads of the rotating shaft. The Ag/AgCl/TiO₂ coupled photocatalyst module is displayed in Fig. 1a. The highly specific surface area Ag/AgCl/TiO₂-coupled photocatalytic cylinder was adapted for structural strength and flow-field design. The assembly process of the Ag/AgCl/TiO₂ coupled photocatalyst module is described in the following text. First, the stirring rotating shaft is passed through the highly specific surface area AgCl/TiO₂-coupled photocatalytic cylinder, the internal thread is screwed into the circular hole in the lower PLA plate, and then the upper PLA plate is placed in the stirring shaft on the upper surface of the highly specific surface area AgCl/TiO₂-coupled photocatalytic cylinder. Bolts are used to spin the upper surface of the photocatalyst cylinder for the upper PLA plate to be combined tightly with the AgCl/TiO₂-coupled photocatalytic cylinder. Finally, near-ultraviolet light is irradiated to generate photoreduction to prepare a highly specific surface area Ag/AgCl/TiO₂-coupled photocatalytic module.

2.3 Three-dimensional printing of the TiO₂ photocatalyst cylinder

A self-made 3D printer created through FFF was used to print the TiO₂ photocatalyst cylinder. Commercial slicing software can be used to set printing parameters and generate G codes for printing devices by adopting 3D computer-aided design models. In the present study, the printing speed was set to 10 mm/s, the print layer height was 0.14 mm, the print line width was 0.2 mm, the filling degree was 30%, and a print bed temperature of 80 °C was selected. A nozzle with a diameter of 0.4 mm was used for the 3D print trials at a nozzle temperature of 200 °C. The (x, y) expansion factor was 19.87%; the z expansion factor was 25.32%. With regard to the positioning system, the spatial resolution of the z-axis was approximately 100 μm, and that of the x-axis and y-axis was approximately 1000 μm. Due to the brittleness of the 3D printing filament, the filament must be heated and kept at 50 °C before feeding into the FFF heating head to increase the toughness of the 3D printing wire and avoid brittle fracture during the 3D printing process. In the solvent debinding
process, the green compact was immersed into n-hexane at 60 °C for 2 h to dissolve and remove the wax and open the pores. At this time, high-density polyethylene was used to maintain the shape of the green compact. Thermal debinding was conducted after solvent debinding. Thermal debinding was then conducted for 1 h at 350 and 500 °C to remove any remaining organic matter. After thermal debinding, the green compact was then sintered in a high temperature furnace at 10^{-1} bar and 1200 °C for 0.5 h to form dense TiO\textsubscript{2} photocatalyst cylinders.

### 2.4 Manufacturing of coupled Ag/AgCl/TiO\textsubscript{2}

We used a heterogeneous precipitation reaction to prepare the Ag/AgCl/TiO\textsubscript{2}-coupled photocatalytic structure (Fig. 2). The preparation of the Ag/AgCl/ TiO\textsubscript{2} coupled photocatalyst is
described in the following text. First, atmospheric-pressure plasma (5 kg/cm² of air at 220 V) was used to hydrophilize the surface of the sintered TiO₂ photocatalyst cylinder, which was then immersed in a 2.5 M aqueous NaCl solution. The NaCl solution was allowed to wet the hydrophilic surface of the TiO₂ photocatalyst completely, and the TiO₂ photocatalyst was then immersed in a 0.5 M aqueous AgNO₃ solution to cause a heterogeneous precipitation reaction. The precipitated AgCl film was evenly coated on the surface of the sintered TiO₂ photocatalyst cylinder. After drying for 2 h at 80 °C, and then washed with deionized water several times to remove any residual chemicals from the surface of the cylinder. Next, to increase the strength of the coupling bond between the AgCl film and TiO₂, the AgCl/TiO₂ coupled photocatalyst cylinder was placed in a high-temperature furnace at 430 °C, heated at a heating rate of 5 °C/min for 24 h, and then furnace cooled to room temperature. Subsequently, this cylinder was irradiated with 365-nm ultraviolet light for 5 min to photoreduce AgCl to Ag/AgCl. Finally, we prepared a photocatalyst cylinder coupled with Ag/AgCl/TiO₂ as shown in Fig. 1b. The X-ray diffractometer (BRUKER, D8A) which was operated at incident light with wavelength 1.54056 Å (CuKα) by copper target, scanning angle 20 from 10° to 90°, a scanning rate of 0.1° s⁻¹, was used to compare and analyze the phases of crystalline phase of the sintered-TiO₂ and the Ag/AgCl/TiO₂-coupled photocatalyst (Joint Committee on Powder Diffraction Standards (JCPDS): 87e0597), AgCl (JCPDS: 85e1355), and anatase-phase TiO₂ (JCPDS: 71e1166).

2.5 Degradation of MB dye by Ag/AgCl/TiO₂ coupled photocatalytic module

The photocatalytic performance of the ceramic module produced through FFF was studied by adopting the Ag/AgCl/TiO₂ coupled photocatalytic module in the degradation of MB dye. MB dye was dissolved in deionized water to a concentration of 10 ppm. An ultraviolet light source (wavelength of 365 nm) and a visible light source (wavelengths of 435, 545, and 612 nm) with an output power of 9 W were used as the light sources for degradation. Figure 3a, b depict the UV and visible light spectrums, respectively. The ultraviolet and visible light sources were used simultaneously because the Ag/AgCl/TiO₂ coupled photocatalyst could absorb ultraviolet and visible light and decompose water simultaneously to produce a large quantity of highly active •OH and •O₂⁻ for photocatalysis. Three blank tests were conducted to determine the photocatalytic abilities of the Ag/AgCl/TiO₂ coupled photocatalyst module and light sources. The setup and testing of the sintered module produced through FFF are described in the following text. A 500-mL glass beaker was used as a reactor and placed on a thermostat to maintain its temperature at 25 °C. In each experiment, the concentration of the MB dye solution was 10 ppm, and the mixture was constantly stirred to increase the collision of dye molecules with the Ag/AgCl/TiO₂ coupled photocatalyst module. Dye degradation was investigated using three experiments. In the first experiment, only the ability of H₂O₂ to degrade MB dye was studied. In the other two experiments, the Ag/AgCl/TiO₂-coupled photocatalyst was hung in the dye solution, and a water lever was placed just above the photocatalysts. Both UV and visible light were placed near the glass beaker, as illustrated in Fig. 4a. In all the experiments, after irradiation, samples were collected regularly to analyze the degradation rate of the MB dye solution. The concentration of the degraded MB dye was measured in accordance with the NIEA W223.50B standard method, in which a spectrophotometer is used to measure the absorbance of a solution at different wavelengths to calculate its American Dye Manufacturers Association value.
2.6 Disinfection of E. coli by Ag/AgCl/TiO$_2$ coupled photocatalytic module

The ability of the sintered module produced through FFF to disinfect E. coli was similar to its ability to degrade MB dye. E. coli cultures with a concentration of 0.6 to 0.8 M were prepared in liquid nutrient broth (lysogen broth) at an optical density of 600 nm. Subsequently, a photocatalytic reaction was conducted for a predetermined duration on the sintered module produced through FFF under ultraviolet light (9 W; 365 nm) and visible light (9 W; 435, 545, and 612 nm) irradiation. Figure 4b depicts the experimental setup for the photocatalytic disinfection of E. coli. The number of bacteria was determined through the establishment of the colony forming number (colony forming unit) by (1) diluting the samples (known dilution ratio), (2) removing 100 μL of the diluted solution, and (3)
smearing the samples on a nutrient agar Petri dish for a 24-h incubation period (37 °C). The bacteria colony then grew, and the number of bacteria in the Petri dish was counted. Each set of the experiment was triple sampled within a predetermined period, cultivated, and counted for accuracy. Blank tests were also conducted for accuracy.

3 Results and discussion

3.1 Characteristics of the 3D printing spool

The microstructures of the sintered TiO₂ and AgCl/TiO₂ photocatalysts are depicted in Fig. 5a, b, respectively. The

Fig. 5 Microstructure of (a) sintered-TiO₂ (b) AgCl/TiO₂ and (c) Ag/AgCl/TiO₂ coupled photocatalyst Ti, O, Cl, and Ag identified using (d) energy dispersive spectroscopy and (e) mapping
average grain size of TiO$_2$ after sintering was approximately 8 μm, and AgCl particles with an average diameter of 20 nm were scattered on the surface of the filament, and the presence of Ag on the AgCl surface was identified through energy dispersive spectroscopy (EDS) and a mapping analysis (Fig. 5c, d). Figure 6 depicts the X-ray diffraction results obtained for the sintered TiO$_2$ and Ag/AgCl/TiO$_2$ coupled photocatalysts. According to the JCPDS database, the diffraction angles (with Miller indices in parentheses) of the sintered TiO$_2$ were 25° (101), 38° (004), 48° (200), 54° (105), and 55° (201). The diffraction angles of the Ag/AgCl crystals were 28° (111), 32° (200) and 46° (220). Moreover, the reduced form of the Ag clusters exhibited a diffraction angle of 38° (111).

3.2 Degradation of methyl blue dye

In the 120-min blank test without light irradiation (only the Ag/AgCl/TiO$_2$ coupled photocatalyst module was used), the degradation rate was less than 2%, which indicates that the Ag/AgCl/TiO$_2$ photocatalyst can only be activated under light irradiation. Figure 7 displays the concentration–time relationships for three types of photocatalysis: 10 ppm of MB + 10 mM hydrogen peroxide + the photocatalyst module (reaction A), 10 ppm of MB + the photocatalyst module (reaction B), and 10 ppm of MB + 10 mM hydrogen peroxide (reaction C). In this figure, C represents the concentration of MB dye at time t, and $C_0$ represents the initial concentration.

![Fig. 6 X-ray diffraction patterns of (a) TiO$_2$ and (b) the Ag/AgCl/TiO$_2$ coupled photocatalyst](image)

![Fig. 7 Degradability of MB dye performed on different scales. (a) Concentration variation over time; (b) concentration logarithm in relation to initial concentration over time; (c) degradation over time (residual concentration to initial concentration)](image)
concentration of 10 mg/L. In this study, the reaction rate followed first-order (or quasi–first order) kinetics [36]; thus, the equation \( \ln \left( \frac{C}{C_0} \right) = k_{\text{app}} \times t \), where \( k_{\text{app}} \) is the apparent rate constant, which represents the degradation rate of MB dye, can be used to determine the catalytic performance. The \( k_{\text{app}} \) values of MB dye in reactions A, B, and C were 0.03754, 0.01149, and 0.004635 min\(^{-1}\), respectively. Figure 8b depicts the hyperbolic relationship for MB dye degradation \( (\frac{C}{C_0} = 1 - t/(a + bt) \text{ or } t/[1 - (C/C_0)] = a + bt \), where \( a \) and \( b \) are constants related to catalytic properties). The values of correlation coefficient \( R^2 \) (\( a \), \( b \)) for reactions B and C were 0.9993 (6.777, 0.9423) and 0.9944 (40.28, 1.004), respectively. The \( R^2 \) values of the reactions were greater than 0.99, which indicates that the tests performed were more likely to accord with the hyperbolic kinetics relations than pseudo-first-order kinetics. When immersed into an aqueous MB dye solution containing 10 mM hydrogen peroxide, the Ag/AgCl/TiO\(_2\) coupled photocatalyst almost completely degraded MB dye within 100 min (99% degradation). Figure 8 illustrates the mechanism through which the Ag/AgCl/TiO\(_2\) coupled photocatalyst degraded the MB dye. The degradation was related to the formation of strong oxidizing free radicals, such as \( \text{O}_2^- \), on account of the interactions of electrons (e\(^-\)) with surface \( \text{O}_2^- \) atoms. The electron holes (h\(^+\)) of AgCl can react with OH\(^-\) to generate OH\(^-\) radicals. \( \text{O}_2^- \) and \( \text{OH}^- \) are strong oxidants that can decompose MB dye (an organic compound) into \( \text{CO}_2 \) and water. In addition, some electron holes may react with AgCl and produce Ag\(^+\) and ClO\(^-\), where Ag\(^+\) accepts electrons from the conduction band and forms Ag atoms and Ag clusters, which prevents further catalysis by AgCl. Cl\(^0\) is also a strong oxidant and can decompose MB dye to generate \( \text{CO}_2 \), \( \text{H}_2\text{O} \), and Cl\(^-\). Moreover, \( \text{H}_2\text{O}_2 \) can increase the formation of OH\(^-\) free radicals and thus the degradation of MB dye. The surface plasmon resonance reaction of the Ag cluster on AgCl may absorb visible light intensively, thus leading to the increased production of Ag\(^+\) and e\(^-\), with some Ag\(^+\) and Cl\(^-\) materials combining to reform AgCl. Additional, most of the electrons can flow from TiO\(_2\) to AgCl to Ag clusters, mainly because the Fermi level of TiO\(_2\) (4.89 eV) is higher than that of AgCl (4.6 eV) and Ag clusters (4.28 eV). Therefore, Ag clusters have too many electrons, while TiO\(_2\) has too many holes, so the recombination of electrons and holes of Ag/TiO\(_2\) can be prevented, which is beneficial to improve the performance of the photocatalyst. This phenomenon results in a highly stable and repeatable condition under which the reuse of this photocatalyst is feasible. Under UV and visible light conditions with five cycles of reuse, when the Ag/AgCl/TiO\(_2\)-coupled photocatalyst (cleaned with distilled water and air-dried before each use) was used, the degradability remained at 94%, as illustrated in Fig. 9. This module therefore has high stability and durability.

### 3.3 Disinfection of E. coli

A photograph of the process of disinfecting E. coli by using the module produced through FFF is displayed in Fig. 10. Figure 11a presents hyperbolic relationship between time and the number of colonies formed of different types of E. coli \( (\frac{C}{C_0} = 1 - t/(a + bt) \text{ or } t/[1 - (C/C_0)] = a + bt) \). The values of \( a \), \( b \), and \( R^2 \) for the disinfection of E. coli were 2.255, 0.9868, and 0.9995.
respectively. Almost all the *E. coli* was eliminated in 120 min when the Ag/AgCl/TiO₂ coupled photocatalyst was used. The disinfection efficiency is presented in terms of percentage in Fig. 11b. The mechanism of *E. coli* disinfection may be related to the generation of silver atoms or free radicals when ultraviolet or visible light photons hit the photocatalyst. When silver atoms come into contact with *E. coli*, some phosphoryl amino acids (such as phosphoryl tyrosine) are dephosphorylated, which results in a change in or the stoppage of the original function of the protein; thus, the growth rate of *E. coli* is reduced. The generated free radicals act as strong oxidants and can damage the cell wall, thereby causing essential substances (such as protein, glucose, and potassium ions) to leak from the cytoplasm into the external environment. Thus, these radicals may severely reduce cell membrane potential, adenosine triphosphate levels, and cell membrane permeability, which may lead to dysfunction or death. Silver nanoparticles may penetrate the cell membrane and bind to the thiol groups of certain enzymes (such as dehydrogenase) in the cell, thereby stopping the function of these enzymes and inactivating the basic metabolism of the cell. In a humid environment, Ag⁺ and electrons may be released from Ag clusters and react with O₂ in water to form •O₂⁻, H₂O₂, or •OH. These strong free radicals can effectively inhibit the metabolism of most cells. When Ag⁺ interacts with bacteria, it may combine with the sulfhydryl group (-SH) in the protein, thereby breaking the original disulfide bond (-S–S-) into a denatured state (-SAg). Ag⁺ eventually stops all reactions related to cell respiration or electron transport, which results in cell death. After cell destruction, Ag⁺ is released, which results in the death of additional cells. This process enables Ag/AgCl/TiO₂ to disinfect bacteria repeatedly and effectively. In the blank test (no light radiation), Ag/AgCl/TiO₂ had no effect on the growth of *E. coli*, which indicates that photons play a role in the activation reaction of Ag/AgCl/TiO₂ [37, 38].

**4 Conclusions**

We fabricated the Ag/AgCl/TiO₂ coupled photocatalytic with a specific surface area of 748 mm²/g by 3D printing a ceramic module produced through FFF. The photocatalytic
ability of the Ag/AgCl/TiO₂ coupled photocatalytic module to degrade MB dye and disinfect E. coli under ultraviolet and visible light irradiation was also studied. This module is suitable for degrading MB dye and disinfecting E. coli within a few minutes to a few hours, depending on the specific surface area of the module. After five cycles of repeated use, the module’s ability to degrade dyes and bacteria remains high (95%). A module based on Ag/AgCl/TiO₂ coupled photocatalyst produced through FFF has broad application prospects as a photocatalyst for degrading pollutants because of its effectiveness, reliability, and structural durability.

Author contribution All the authors have contributed equally to the paper.

Funding This study was supported by the National Science Council, Taiwan (MOST109-2221-E-032-021).

Declarations

Ethics approval Complied with ethical standards.

Consent to participate and consent for publication All authors agree to contribute and publish the article.

Competing interests The authors declare no competing interests.

References

1. Huang ST, Jiang YR, Chou SY, Dai YM, Chen CC (2014) Synthesis, characterization, photocatalytic activity of visible-light-responsive photocatalysts BiOCl/BiOBr by controlled hydrothermal method. J Mol Catal A: Chem 391(1):105–120. https://doi.org/10.1016/j.molcata.2014.04.020
2. Low J, Yu J, Jaroniec M, Wageh S, Al-Ghandi AA (2017) Hetero-junction photocatalysts. Adv Mater 29(20):1601694. https://doi.org/10.1002/adma.201601694
3. Fujisima A, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. Nature 238:37–38. https://doi.org/10.1038/238037a0
4. LibanorI, Giraldo TR, Longo E, Leite ER (2009) Effect of TiO₂ surface modification in Rhodamine B photo degradation. J Sol Gel Sci Technol 49(1):95–100. https://doi.org/10.1007/s10971-008-1821-1
5. Choi M, Shin KH, Jang J (2010) Plasmonic photocatalytic system using silver chloride/silver nanostructures under visible light. J Colloid Interface Sc 341(1):83–87. https://doi.org/10.1016/j.jcis.2009.09.037
6. Kakuta N, Goto N, Okita H, Mizushima T (1999) Silver brome as a photocatalyst for hydrogen generation from CH₃OH/H₂O solution. J Phys Chem B 103(29):5917–5919. https://doi.org/10.1021/jp990287g
7. Guo JF, Ma BW, Yin AY, Fan KN, Dai WL (2012) Highly stable and efficient Ag/AgCl/TiO₂ photocatalyst: preparation, characterization, and application in the treatment of aqueous hazardous pollutants. J Hazard Mater 211–212:77–82. https://doi.org/10.1016/j.jhazmat.2011.11.082
8. Sohrabnezhad S, Pourahmad A (2012) As-synthesis of nanostructure AgCl/Ag/MCM-41 composite. Spectrochim Acta A Mol Biomol Spec trosc 86:271–275. https://doi.org/10.1016/j.saa.2011.10.035
9. Yang Q, Hu M, Guo J, Ge Z, Feng J (2018) Synthesis and enhanced photocatalytic performance of Ag/AgCl/TiO₂ nano composites prepared by ion exchange method. J Materiomics 4(4):402–411. https://doi.org/10.1016/j.jmat.2018.06.002
10. Hu C, Peng TW, Hu XX, Nie YL, Zhou XF, Qu JH, He H (2010) Plasmon-induced photodegradation of toxic pollutants with Ag–AgI/Al₂O₃ under visible-light irradiation. J Am Chem Soc 132(2):857–862. https://doi.org/10.1021/ja907792d
11. Xu YG, Xu H, Li HM, Xia JX, Liu CT, Liu L (2011) Enhanced photocatalytic activity of new photocatalyst Ag/AgCl/ZnO. J Alloys Compd 509(7):3286–3292. https://doi.org/10.1016/j.jallcom.2010.11.193
12. Luo GQ, Jiang XJ, Li MJ, Shen Q, Zhang LM, Yu HG (2013) Facile fabrication and enhanced photocatalytic performance of Ag/AgCl/rGO heterostructure photocatalyst. ACS Appl Mater Inter faces 5(6):2161–2168. https://doi.org/10.1021/am303225n
13. Granbohm H, Singh VK, Ge Y, Hannula S-P (2017) Effect of graphene oxide loading in GO/SiO₂/Ag/AgCl photocatalyst. Int J Nanotechnol 14:87–99. https://doi.org/10.1504/ijnnt.2017.082448
14. Panchal P, Meena P, Neher SP (2021) A rapid green synthesis of Ag/AgCl/NC photocatalyst for environmental applications. Environ Sci Pollut Res 28:3972–3982. https://doi.org/10.1007/s11356-020-11834-5
15. Viswanathan VP, Divya KS, Dubal DP, Adarsh NN, Mathew S (2021) Ag/AgCl/CoMIL-88A(Fe) heterojunction ternary composites: towards the photocatalytic degradation of organic pollutants. Dalton Trans 50:2891–2902. https://doi.org/10.1039/D0DT03147J
16. Padervand M, Hajiahmadi S (2022) Ag/AgCl@Tubular g-C3N4 nanostucture as an enhanced visible light photocatalyst for the removal of organic dye compounds and biomedical waste under visible light. J Photochem Photobiol, A 425:113700. https://doi.org/10.1016/j.jphotochem.2021.113700
17. Pang Du, Xie H, Gao Y, Li Y, Zhao Y, Yang C (2022) Ag/AgCl/BiO2-x activated persulfate to degrade rhodamine B under visible light. J Mater Sci Mater Electron 33:5776–5789. https://doi.org/10.1007/s10854-022-07762-4
18. Li Y, Yin W, Li M, Zhang J, Chen L (2022) Multi-component Ag/AgCl/Bi2O3/BiFeO3 for the sunlight-induced photocatalytic degradation. J Environ Chem Eng 10(2):107280. https://doi.org/10.1016/j.jece.2022.107280
19. Zhang J, Liu X, Suo X, Li P, Liu B, Shi H (2017) Facile synthesis of Ag/AgCl/TiO₂ plasmonic photocatalyst with efficiently antibacterial activity. Mater Lett 198:164–167. https://doi.org/10.1016/j.matlet.2017.04.029
20. Liu W, Chen D, Yoo S, Cho S (2013) Hierarchical visible-light response Ag/AgCl/TiO₂ plasmonic photocatalysts for organic dye degradation. Nanotechnology 24(40):405706. https://doi.org/10.1088/0957-4484/24/40/405706
21. Shah Z, Wang JS, Ge X, Wang C, Mao W, Zhang S (2015) Highly enhanced plasmonic photocatalytic activity of Ag/AgCl/TiO₂ by CuO co-catalyst. J Mater Chem A 3(7):3568–3575. https://doi.org/10.1039/c4ta05777e
22. Ge Z, Ji Y, Qiu Y, Chong X, Feng J, He J (2018) Enhanced thermoelectric properties of bismuth telluride bulk achieved by telluride-spilling during the spark plasma sintering process. Scripta Mater 143:90–93. https://doi.org/10.1016/j.scriptamat.2017.09.020
23. Yang L, Ma X, Zhang W, Gen W (2016) Ag/AgCl/TiO₂/organic rectorite/quaternized chitosan microspheres: an efficient and environmental photocatalyst. J Appl Polym Sci 134:44601. https://doi.org/10.1002/app.44601
24. Guan X, Lin S, Lan J, Shang J, Li W, Zhan Y, Xiao H, Song Q (2019) Fabrication of Ag/AgCl/ZIF-8/TiO₂ decorated cotton fabric as a highly efficient photocatalyst for degradation of organic
dyes under visible light. Cellulose 26(12):7437–7450. https://doi.org/10.1007/s10570-019-02621-8

25. Nakhostin Panahi P, Mohajer S, Rasoulifard MH, Farajmand B (2020) Synthesis of Ag/AgCl/TiO2 nanocomposite and study of photocatalytic activity in VOCs removal from gas phase. Int J Environ Anal Chem. https://doi.org/10.1080/03067319.2020.1751146

26. Bao N, Miao X, Xinde Hu, Zhang Q, Jie X, Zheng X (2017) Novel synthesis of plasmonic Ag/AgCl@TiO2 continues fibers with enhanced broadband photocatalytic performance. Catalysts 7(4):117. https://doi.org/10.3390/catal7040117

27. Yang L, Wang F, Shu C, Liu P, Zhang W, Hu S (2016) An in-situ synthesis of Ag/AgCl/TiO2/hierarchical porous magnesium material and its photocatalytic performance. Sci Rep 6:21617. https://doi.org/10.1038/srep21617

28. Ghasemi Z, Abdi V, Sourinejad I (2020) Green fabrication of Ag/AgCl@TiO2 superior plasmonic nanocomposite: biosynthesis, characterization and photocatalytic activity under sunlight. J Alloys Compd 841:155593. https://doi.org/10.1016/j.jallcom.2020.155593

29. Vidakis N, Petousis M, Maniadi A, Koumoumas E, Liebscher M, Tzounis L (2020) Mechanical properties of 3D-printed acrylonitrile-butadiene-styrene TiO2 and ATO nanocomposites. Polymers 12(7):1589. https://doi.org/10.3390/polym12071589

30. Sangiorgi A, Gonzalez Z, Ferrandez-Montero A, Yus J, Sanchez-Herencia AJ, Galassi C, Sanson A, Ferrari B (2019) 3D printing of photocatalytic filters using a biopolymer to immobilize TiO2 nanoparticles. J Electrochem Soc 166(5):H3239–H3248. https://doi.org/10.1149/2.034190jes

31. Vidakis N, Petousis M, Maniadi A, Koudoumas E, Liebscher M, Tzounis L (2020) Mechanical properties of 3D-printed acrylonitrile–butadiene–styrene TiO2 and ATO nanocomposites. Polymers 12(7):1589. https://doi.org/10.3390/polym12071589

32. Brounstein Z, Yeager CM, Labouriau A (2021) Development of antimicrobial PLA composites for fused filament fabrication. Polymers 13(4):580. https://doi.org/10.3390/polym13040580

33. Sevastiaki M, Suchea MP, Kenanakis G (2020) 3D printed fully recycled TiO2-polystyrene nanocomposite photocatalysts for use against drug residues. Nanomaterials 10(11):2144. https://doi.org/10.3390/nano10112144

34. Yang L, Wang F, Shu C, Liu P, Zhang W, Hu S (2016) An in-situ synthesis of Ag/AgCl/TiO2/hierarchical porous magnesium material and its photocatalytic performance. Sci Rep 6:21617. https://doi.org/10.1038/srep21617

35. Sangiorgi A, Gonzalez Z, Ferrandez-Montero A, Yus J, Sanchez-Herencia AJ, Galassi C, Sanson A, Ferrari B (2019) 3D printing of photocatalytic filters using a biopolymer to immobilize TiO2 nanoparticles. J Electrochem Soc 166(5):H3239–H3248. https://doi.org/10.1149/2.034190jes

36. Ghasemi Z, Abdi V, Sourinejad I (2020) Green fabrication of Ag/AgCl@TiO2 superior plasmonic nanocomposite: biosynthesis, characterization and photocatalytic activity under sunlight. J Alloys Compd 841:155593. https://doi.org/10.1016/j.jallcom.2020.155593

37. Vidakis N, Petousis M, Maniadi A, Koumoumas E, Liebscher M, Tzounis L (2020) Mechanical properties of 3D-printed acrylonitrile-butadiene-styrene TiO2 and ATO nanocomposites. Polymers 12(7):1589. https://doi.org/10.3390/polym12071589

38. Brounstein Z, Yeager CM, Labouriau A (2021) Development of antimicrobial PLA composites for fused filament fabrication. Polymers 13(4):580. https://doi.org/10.3390/polym13040580

39. Sevastiaki M, Suchea MP, Kenanakis G (2020) 3D printed fully recycled TiO2-polystyrene nanocomposite photocatalysts for use against drug residues. Nanomaterials 10(11):2144. https://doi.org/10.3390/nano10112144

40. Brounstein Z, Yeager CM, Labouriau A (2021) Development of antimicrobial PLA composites for fused filament fabrication. Polymers 13(4):580. https://doi.org/10.3390/polym13040580

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.