Antibacterial properties of Ag/TiO$_2$/PDA nanofilm on anodized 316L stainless steel substrate under illumination by a normal flashlight

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ABSTRACT

The demand of medical materials for rapid and efficient elimination of bacteria has seen a dramatic surge over the past few years. In this study, antibacterial nanofilms with reactive oxygen species were generated by photocatalysis. To prepare these nanofilms, Ag and amorphous TiO$_2$ nanoparticles decorated on polydopamine (PDA) were coated on three-dimensional (3D) nanopore arrays, which was fabricated on a substrate of anodized stainless steel. All the antibacterial tests were conducted with a household flashlight, which may be considered as a practical approach for antibacterial materials. The photoelectrochemical property of the 3D Ag/TiO$_2$/PDA nanofilm on 316L stainless steel (Ag/TiO$_2$/PDA SS) was about 15 times higher than that of the annealed Ag/TiO$_2$/PDA SS, and consequently, it exhibited higher antibacterial activity. The enhanced photoelectrochemical property is attributed to the successful separation of electrons (amorphous TiO$_2$) and holes (Ag nanoparticles). Further, when a plate containing 3D Ag/TiO$_2$/PDA SS was irradiated with visible light just for 10 min, it immediately destroyed the bacteria in 10$^6$ CFU/mL without any bacterial colony. After five weeks, there were still no bacterial colonies in the plate corresponding to Ag/TiO$_2$/PDA SS under visible light, while Ag/TiO$_2$/PDA SS in dark had a negligible effect on the bacteria, i.e., the antibacterial mechanism through direct contact and ion dissolution was not efficient. The excellent antibacterial properties of 3D Ag/TiO$_2$/PDA SS illuminated by flashlight provides an efficient, facile, and cost-effective technique for the development of antibacterial medical materials to meet the increasing demand of eliminating bacterial infections.
Introduction

Recent years have witnessed increasing outbreaks of biomaterial-related infections such as Novel Coronavirus, Listeria monocytogenes and salmonella infections [1–3]. This has caused widespread concern because a growing number of patients are under death risk or under financial burden due to such infections [4–6]. *Escherichia coli* (*E. coli*) can be pathogenic under certain conditions, and the occurrence and prevalence of *E. coli* are worldwide. Prevent spreading germs by cleaning and disinfection are effective methods. However, the effect can remain for a period after disinfection. It will be a very high cost to clean and disinfect the things that people have frequent contact with over and over again. Thus, the sterilization experiment on the surface of antibacterial materials against *E. coli* rapidly in real time is one of the most popular, and most studied, tests around [4–6]. According to the surging demand of antibacterial medical materials [4, 5, 7, 8], the surface modification of 316L stainless steel (SS), which is widely applied in medical field, has garnered considerable attention to enhance its antibacterial property [9–11].

Presently, the antibacterial mechanism of 316L SS is mainly based on the dissolution of Ag, Cu, or Zn ions [9–12], which is limited by several factors such as the safe range of ion concentration, competition between rates of ion dissolution and bacterial proliferation and the antibacterial period [13–16]. Photocatalysis is a highly efficient and inexpensive technique to inhibit and kill the bacteria [17–20]. It is based on the photochemical properties of semiconductor photocatalyst to generate reactive oxygen species (ROS), superoxide anion (*O*$_2^-$) radicals under external energy such as the natural energy of sunlight [20–22]. TiO$_2$, a wide band gap semiconductor (3.2 eV), is generally used as a photocatalyst in the presence of ultraviolet (UV) radiation [23, 24]. However, it is still restricted by the large band gap structure and very high recombination rate of photogenerated electron–hole pairs [25]. Coupling TiO$_2$ with Ag nanoparticle (TiO$_2$@Ag) is an efficient way to improve its photocatalytic property under visible light [19, 26, 27]. It is well known that the photocatalytic activity depends on the utilization of light energy as well as on the separation of photogenerated electrons and holes [28]. Several existing studies have demonstrated that an thin amorphous TiO$_2$ nanolayer can not only increase the specific surface area to enhance light harvesting but also improves the separation of photogenerated electrons and holes, thereby improving the photocatalytic activity [29–31]. Wu et al. fabricated Ag/TiO$_2$ nanoparticles through dopamine-assisted process, which exhibited high activity for *Escherichia coli* (*E. coli*) and Bacillus subtilis bacteria under visible light [32]. The decrease in the thickness of the coating accelerates the transformation of photo-generated carriers. Polydopamine (PDA) [9, 33], a biopolymer mimic of mussels, can significantly improve the photocatalytic activity through effective transfer of photoinduced electrons and protons. Further, PDA nanofilms do not alter the morphology of surface coating [34, 35].

Our group has fabricated nanopore arrays on the surface of 316L SS by anodic oxidation [36–38]. The use of anodized 316L SS has received considerable attention for increasing the surface areas, because the inert SS with high corrosion resistance are difficultly corroded [39–41]. In this study, we have synthesized a three-dimensional (3D) Ag/TiO$_2$/PDA nanofilm using Ag-decorated amorphous TiO$_2$ nanolayer as light harvester and PDA as transformation interface. This nanofilm was formed on anodized 316L SS to effectively inhibit or kill bacteria under visible light, which is attributed to the following two factors. Firstly, the Ag/TiO$_2$ nanocomposite efficiently separated the visible photogenerated electron–hole pairs. Secondly, the carriers were transferred to PDA. The visible light required in the antibacterial experiment was obtained from a normal flashlight, which means these antibacterial materials can be used in infrastructure construction and home products under Civilian LED lights, let alone the sunlight. The morphology and material property of the surface of 316L SS are also investigated. Further, the antibacterial rate and the formation mechanism of 3D Ag/TiO$_2$/PDA under visible light are theoretically analyzed to provide clear insights on photocatalytic antibacterial activities.

Materials and methods

The 316L SS sheet was cut into sheets (10 × 10 × 1 mm) to ease the grinding and cleaning process. All the chemicals were of analytical grade, which were purchased from Sino pharm Chemical Reagent Co., Ltd and used as is without further
puriﬁcation. De-ionized (DI) water was used in this experiment.

**Preparation of Ag/TiO$_2$/PDA nanofilm on 316L SS**

**Preparation of three-dimensional nanopore arrays on 316L SS**

The nanopore arrays were fabricated on the surface of 316L SS by two step anodization, which has been described in our previous reports [37, 38]. Typically, 316L SS sheet was mechanically polished and cleaned in ethanol, then in double distilled water (DDW) by ultrasonic cleaner. At the ﬁrst anodization experiment, 316L SS was electropolished in ethylene glycol (EG) solution containing 5 vol % perchloric acid at 20 V for 20 min. The electropolished sheets was used in the second anodization experiment in a 0.3 mol/L sodium dihydrogen phosphate solution at 5/C176C and anodized at 30 V for 20 min. The two-step anodization can directly produce the nanopore arrays on the surface of the anodized sheet.

**Preparation of PDA nanofilm on 316L SS**

Ag/TiO$_2$/PDA nanofilms were fabricated on 316L SS at normal temperature and pressure with an inexpensive technique. Typically, 316L SS sheets were immersed in a mixture solution containing 4 mg/mL DA + 20 mmol/L Tris + DI water (pH 8.5) for 6 h to form PDA coating.

**Preparation of TiO$_2$/PDA nanofilm on 316L SS**

The sheets were then washed with DI water and dried in an oven at 50 °C for 1 h. We used 0.01 mol/L (NH$_4$)$_2$TiF$_6$ solution in a three-electrode electrochemical cell with working electrode of 316L SS sheets, reference electrode of Ag/AgCl, and counter electrode of platinum wire.

**Preparation of Ag/TiO$_2$/PDA nanofilm on 316L SS**

The clean and dried 316L SS sheets with TiO$_2$/PDA coating were immersed in 0.01 mol/L AgNO$_3$ solution for 5 min to form Ag nanoparticles.

**Preparation of annealed Ag/TiO$_2$/PDA nanofilm on 316L SS**

The sheets were marked as T-1, T-2, T-3, and T-4, which represented Ag/TiO$_2$/PDA sheets deposited through 10, 20, 30, and 40 cycles, respectively, in Ti ion solution without annealing treatment. When these sheets were annealed at 550 °C for 3 h in a tube furnace purged with pure argon ﬂow, they were marked as AT-1, AT-2, AT-3, and AT-4, respectively.

**Photoelectrochemical properties of 316L SS sheets**

Photoelectrochemical properties were tested with amperometric i-t curve in the three-electrode electrochemical system equipped with a xenon lamp (500 W). A quartz reactor with electrodes immersed in 20 mL of 0.1 mol/L phosphate-buffered saline (PBS; 7.4) was placed at a distance of 15 cm from the xenon lamp, and the sheets with an area of ~ 1 cm$^2$ were exposed to repeated on/off visible light illumination (time step of 50 s).

**Antibacterial tests under illumination by a normal ﬂashlight**

The antibacterial activity of the 316L SS sheets against Gram-negative E. coli (CCTCC AB 90,054) bacteria was studied by the plate count method and the incubation temperature was 37 °C. To further promote the practical application of this antibacterial material, a household ﬂashlight was used in all the antibacterial tests with green XML2 light emitting diode (LED). The maximum power of this LED bulbs was about 12 W with maximum 1200 lm.

**The plate count method and the counting of antibacterial ratio of Ag/TiO$_2$/PDA sheets**

After the culture end, the sheets were rinsed several times with sterilized 1 mL Lysogeny broth (LB) to collect all the bacteria on the sheets. The concentration of bacteria suspensions in the 1 mL LB was measured in a culture dish coated with 0.1 mL bacteria suspension by plate count method. This implies that the maximum concentration gradient was used in all the antibacterial tests.
The number of bacterial colonies in the samples was calculated to assess the antibacterial rate, which is expressed as follows:

\[
\text{Antimicrobial rate} = \left( \frac{A - B}{A} \right) \times 100\%,
\]

where \( A \) and \( B \) are the number of bacterial colonies in the control and test sheets, respectively. For avoiding experimental errors, each experimental group was evaluated three times.

**The survival rate of bacteria on anodized 316L SS sheets**

As anodized 316L SS itself had proper photocatalytic properties, the survival rate of bacterial on control samples, anodized 316L SS sheets, was investigated under illumination by a normal flashlight in this work.

The typical test is as follows: the control samples, anodized 316L SS, were covered with 0.1 mL bacterial suspensions (\(10^6\) CFU/mL) in dark and/or under visible light irradiation, ranging from 10 min to 24 h.

**The effect of irradiation time on the antibacterial properties of Ag/TiO\(_2\)/PDA sheets**

The typical antibacterial test is as follows: 0.1 mL bacterial suspensions (\(10^6\) CFU/mL) was dropped on the test samples of Ag/TiO\(_2\)/PDA sheets and control samples of anodized sheets. The Ag/TiO\(_2\)/PDA sheets and control sheets covered with bacteria solution were put in the quartz cup and then incubated at 37 °C for several times (10 min, 15 min, 0.5 h, 1 h, 2 h, 3 h), where one group was placed in dark and another was irradiated by visible light.

**The antibacterial persistence of Ag/TiO\(_2\)/PDA sheets**

Antibacterial test, as described above, were repeated 5 times on the same samples in dark and/or under visible light irradiation for 3 h. After each antibacterial test, the samples were cleaned in DDW to remove the residue by ultrasonic cleaner and then immersed in PBS solution for 7 days until next repeated experiment.

**Results and discussion**

**Evaluation of photoelectrochemical properties**

Figure 1 shows the photoelectrochemical response of the annealed (AT-1, AT-2, AT-3, and AT-4) and unannealed sheets (T-1, T-2, T-3, and T-4) in PBS under visible light. The variation of photocurrent density under repeated on/off visible light illumination (time step = 50 s) is shown in Fig. 1a–c, and its value for different samples is shown in Fig. 1d. As the Figs.S1 and S2 show, the photocurrent densities of T-3 photoelectrodes were to be maximum at the bias of \(-0.8\) V. Then, the bias of \(-0.8\) V could be used in the subsequent study to measure the photocatalytic properties of T-3 photoelectrodes. The applied potential of \(-0.8\) V (Fig. 1a) induced the optimal photocurrent densities of 0.21, 0.29, 0.42, and 0.22 \(\mu\)A cm\(^{-2}\) in AT-1, AT-2, AT-3, and AT-4, respectively, which indicates that AT-3 involved the optimal condition of TiO\(_2\) deposition on the annealed sheets through 30 cycles. Figure 1b shows that the optimal photocurrent density of T-3 that involved the same condition of deposition is 6.3 \(\mu\)A cm\(^{-2}\), which is evidently higher than that of T-1, T-2, and T-4. It is interesting to observe the difference between the two optimal sheets with and without annealing under the same condition. Figure 1c shows that the photocurrent of T-3 is about 15 times higher than that of AT-3.

Figure 2 compares the XRD patterns of T-3 and AT-3. In Fig. 2a, the two sheets exhibit the same diffraction peaks at 43.5°, 50.7°, and 74.7°, which represent the austenite crystal phase of SS (JCPDS 031-0619). No characteristic peaks of TiO\(_2\) deposited on the unannealed sheets is observed here, but the element distribution shown in Fig. S3 confirmed the presence of Ti element, which implies that TiO\(_2\) exhibits amorphous phase. For AT-3, no diffraction peak of TiO\(_2\) could be detected due to the permeation of Ti atoms into stainless steel substrate for the same lattice constant of titanium and the iron. The unannealed sheets display the characteristic diffraction peaks of Ag crystal at 38.1°, 44.3°, 64.4°, and 77.5° (JCPDS 04-0783). The XRD patterns of annealed sheets showed three characteristic peaks of austenite phase in Fig. 2a, while the peak in red frame amplified in Fig. 2b could be fitted by the combination of two peaks centered at 43.49° and 43.62°. Comparing to the independence of the peaks of Ag crystal in
unannealed samples T-3, the observed shift of peaks of Ag crystal in annealed samples AT-3 suggested that Ag atoms had entered the austenite crystal lattice.

Figure 1  Photocurrent of a AT-1, AT-2, AT-3, AT-4, b T-1, T-2, T-3, T-4, and c AT-3 and T-3 (c). d Histogram of photocurrent for all the samples.

Figure 2  XRD patterns of AT-3 and T-3.

For comparison with the anodized sheets (Fig. 3a), the thin film of TiO₂/PDA was coated on the nanostructure of 316L SS, as shown in Fig. 3b. The individual nanoparticles of Ag are uniformly...
dispersed on the 3D TiO\(_2\)/PDA nanolayer formed on the nanopore arrays on 316L SS in Fig. 3c, where the average particle size is ca. 12 nm. After annealing treatment, the nanofilm structure was destroyed and was replaced by a coating of aggregate nanoparticles on the 3D nanostructure of 316L SS, as shown in Fig. 3d. The TEM image of Ag/TiO\(_2\)/PDA coating exfoliated from the 316L SS substrate is shown in Fig. 4a. The bottom light toned layer of this image corresponds to the PDA coating, while the middle mid-toned layer represents the thin amorphous TiO\(_2\). The dark Ag nanoparticles with varying sizes were dispersed on the TiO\(_2\)/PDA coating. The high-resolution TEM (HRTEM) image for a selected region of Fig. 4a with dark and light nanoparticles overlapping each other (Fig. 4b) shows that lattice spacing of the dark nanoparticles is ca. 0.236 nm, which can be attributed to the (111) crystal face of Ag. The light nanoparticles without pronounced lattice fringes represent amorphous TiO\(_2\). According to the XRD analysis in this work and the diffusion trait of Ag in TiO\(_2\) nanofilm [42–44], Ag particles started to agglomerate and some Ag nanoparticles diffused into the TiO\(_2\) nanofilm during the calcination. The heat treatment decreased the distance between Ti atoms and transformed the amorphous TiO\(_2\) nanofilm to

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**Figure 3** SEM images of a anodized SS, b TiO\(_2\)/PDA coating on anodized stainless steel, c AT-3, and d T-3. Inset in c shows the size distribution of Ag nanoparticles in T-3.

**Figure 4** a TEM and b HRTEM image of Ag/TiO\(_2\)/PDA nanofilm.
crystalline nanoparticles [44]. Meanwhile, calcination caused the carbonization of PDA, leading to the inlaying of a large number of graphite nanoparticles in the coating [45, 46]. Figure 5 shows a schematic of the synthetic processing of Ag/TiO₂/PDA nanofilm, where the annealing treatment causes the destruction of nanofilm structure of Ag/TiO₂/PDA and nanoparticles of Ag, TiO₂ and graphite are non-uniformly distributed on the nanopore arrays on 316L SS. These aggregated nanoparticles forming a thin layer can accelerate the recombination of photogenerated electrons and holes. The analyzed morphology and structure is consistent with the higher phot electrochemical properties of T-3 than that of annealed sheets.

Figure 6 shows the UV–visible diffuse reflectance spectra of Ag/TiO₂/PDA on the 3D nanopore arrays of 316L SS and that of the anodized 316L SS. It is clear that the 316L SS modified with Ag/TiO₂/PDA coating exhibits a stronger visible light absorption. The band gap energy (E₉) can be calculated according to the Kubelka–Munk equation, 
\[ \alpha(h\nu)^n = A(h\nu - E_g), \]
where \( \alpha \) is the absorption coefficient, \( A \) is a constant dependent on the material, \( h\nu \) is the incident photon energy, \( E_g \) is the band gap, and the exponent ‘n’ depends on the direct or indirect transition across the band gap. Based on this equation, we obtained a band gap of 2.4 eV.

According to the XRD and TEM characteristics, the schematic energy band and electron transformation of Ag/TiO₂/PDA SS is shown in Fig. 7. Under visible light illumination, the electron stimulated by surface plasmon resonance of Ag nanoparticles crosses over the Schottky barrier height and is transferred to the amorphous TiO₂ conduction band. The electron (amorphous TiO₂) and hole (Ag nanoparticles) were successfully separated, which corresponds to the enhancement of photoelectrochemical responsivity. The contribution of PDA nanofilm as plausible support to the photocatalytic mechanism is confirmed by the efficient electron transfer process. Subsequently, some ROS such as hydroxyl radical, hydrogen peroxide, and superoxides are generated, which can destroy the cell wall and membrane of bacterial cell, causing immediate bacterial inactivation [47–49].

**Antibacterial activity of Ag/TiO₂/PDA nanofilm under visible light irradiation**

The Ag NP has shown good antibacterial properties as it contacts with microorganisms through crossing...
cell membranes and disrupting bacterial proteins [13–16]. The application based on the antibacterial mechanisms of Ag NP is limited due to the use of large amount of precious metal and the accompanying leaching. As described in the Fig. 7, the antibacterial mechanism of Ag/TiO$_2$/PDA nanofilm showed that Ag/TiO$_2$/PDA nanofilm generated highly ROS after visible light irradiation [47–49]. The presence of the ROS with hydroxyl groups leads to cell inactivation through oxidative damage of the cell membrane or by the penetration of superoxide anions and hydrogen peroxide into the cells [50]. In order to rule out the antibacterial efficacy of the Ag NP for contacting antibacterial mechanism, the Ag/TiO$_2$/PDA nanofilm and the control samples were tested in dark and/or under visible light irradiation [51].

The major aim of this study is to analyze the antibacterial activity of Ag/TiO$_2$/PDA SS under the
visible light illumination by a flashlight and to evaluate its ability for effective and rapid inhibition or destruction of bacteria. To this end, the effect of visible light illumination on the bacteria surviving on control samples was studied by comparing the control samples with and without irradiation. It is evident from Fig. 8 that the survival rate for control samples illuminated by flashlight significantly decreased as the time increased from 10 min to 24 h as compared to the samples in dark. During the first 3 h of irradiation, the bacteria on the control samples were pretty much unaffected by the flashlight with a survival rate of ca. 85%. After 12 h, the visible light irradiation caused self-destruction of the bacteria, which may be attributed to the photocatalytic performance of Fe$_2$O$_3$ and Fe$_2$O$_3$–Cr$_2$O$_3$ heterojunction according to an earlier study [36]. Hence, the optimal irradiation time of 3 h was applied in the subsequent tests. Figure 9 shows the snapshots of control SS, Ag/TiO$_2$/PDA SS, and annealed Ag/TiO$_2$/PDA SS exposed to visible light for 3 h. After the antibacterial test, no bacterial colonies were present in the plate containing Ag/TiO$_2$/PDA SS, while the number of bacterial colonies in plates containing control SS and annealed Ag/TiO$_2$/PDA SS exceeded the effective colony number of 300 according to the national standard of GB 47,892–2010. This stark contrast in the antibacterial properties of Ag/TiO$_2$/PDA SS and annealed Ag/TiO$_2$/PDA SS can be proved by the difference in the number of bacterial colonies. This result is consistent with the photoelectrochemical properties studies in the previous subsection.

The snapshots of bacterial colonies and the experimentally obtained photo-antibacterial activity of Ag/TiO$_2$/PDA SS vs. the irradiation time (10 min, 15 min, 0.5 h, 1 h, 2 h, 3 h) are shown in Figs. 10 and 11, respectively. The antibacterial rate of Ag/TiO$_2$/PDA SS exposed to the visible light from flashlight is over 99%. Even in the initial 10 min, the Ag/TiO$_2$/PDA SS under visible light illumination starts to kill the bacteria, while the Ag/TiO$_2$/PDA SS in dark exhibits faint inhibition. Earlier studies have demonstrated that photocatalysis can generate ROS such as $^*$OH, $^1$O$_2$, $^*$_OH, $H_2O_2$, which can cause the decomposition of bacteria. This indicates that the enhanced antibacterial activities can be attributed to the photocatalytical properties of Ag/TiO$_2$/PDA nanofilm irradiated by the flashlight. Compared to the earlier reports on SS shown in Table 1, the adhesion time of bacteria on the surface of the samples is normally over 0.5 h as they exhibit inhibition properties. The antibacterial activity of 316L SS under visible light illumination has not been studied before. According to the earlier reports on photocatalysis under UV or visible light irradiation shown in Table 2, Ag/TiO$_2$/PDA SS exhibits optimal

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**Figure 8** Increase in the destructive effect of visible light on the control samples of anodized SS against *E. coli* bacteria.
antibacterial property with 99% antibacterial rate at 10 min in 10⁶ CFU/mL bacterial suspensions.

To further inspect long-term stability of the antibacterial properties of Ag/TiO₂/PDA SS, we conducted repeated antibacterial test on one sample for five weeks under visible light illumination for 3 h. Figure 10 shows the decrease in the antibacterial rate of Ag/TiO₂/PDA SS in dark to ~ 20% after 3 weeks, indicating negligible inhibition properties of Ag/TiO₂/PDA SS with contact antibacterial mechanism. Meanwhile, Ag/TiO₂/PDA SS under visible light irradiation retained its excellent antibacterial properties over the five weeks, whereas the antibacterial mechanism of ion dissolution was no longer useful.

**Conclusion**

The achievement of rapid and long-term antibacterial activity has been a major challenge for antibacterial materials, especially for 316L SS. In this work, we proposed a facile and cost-effective approach to synthesize a Ag/TiO₂/PDA nanofilm on 316L SS, in which Ag nanoparticles decorated with amphoras TiO₂ nanofilm were coating on PDA thin film. Under visible light illumination, the electron stimulated by Ag nanoparticles served as the main visible light absorber was transferred to the amorphous TiO₂ conduction band for an efficient charge carrier separation. The contribution of PDA nanofilm as plausible support to the photocatalytic mechanism is confirmed by the efficient electron transfer process.
Compared to the annealed Ag/TiO$_2$/PDA SS, the unannealed Ag/TiO$_2$/PDA nanofilm not only exhibited a higher photoelectrochemical property under visible light, but also showed more highly efficient, rapid, and stable antibacterial properties.
The future scope of this work involves the intensive investigation of the photo-antibacterial mechanism of Ag/TiO₂/PDA SS based on the effect of ROS on bacteria at the molecular level. We believe that the intermediate PDA layer renders Ag/TiO₂/PDA nanofilm as a favorable antibacterial coating on a wide variety of substrates such as glass, metal alloy, and plastic. It will promise in a broad range of antibacterial material’s application into health and environment.

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Compliance with ethical standards
Conflict of interest The authors declare that they do not have any competing financial interests or personal relationships that could have influenced the work reported in this paper.

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