

Titania-based photocatalysts functionalized on stainless steel and its photocatalytic antibacterial activity

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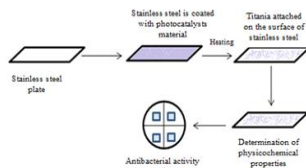
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GRAPICAL ABSTRACT



Schematic representation of the coating of TiO₂-based photocatalysts on stainless steel by using an AFA

ABSTRACT

Owing to the potential environmental applications, photocatalytic reactions occurring on the surface of photoirradiated titanium(IV) oxide (TiO₂) have garnered a wide interest. One of the many usage of TiO₂ as a photocatalyst is in inhibiting bacterial growth. TiO₂ is generally coated onto the surface of a substrate material and the material's photocatalytic antibacterial activity is then investigated. In the present study, TiO₂-based photocatalysts were coated on the surface of stainless steels by using an automatic film applicator (AFA), which is able to produce a uniform coating with controllable thickness and high resistivity. By using this method, it is also possible to directly use TiO₂ powder, instead of using other TiO₂ source that requires crystallization process afterwards. The TiO₂ photocatalysts were firstly prepared by preparing the mixture of the coating process, which consisted of anatase TiO₂ powder, polyvinyl alcohol as the binder, ammonium citrate tribasic as the stabilizer and distilled water, where different compositions of TiO₂ were used. After the coating process by AFA, the samples then underwent heating process at 200 °C. The prepared photocatalysts were characterized by field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared (FTIR) spectroscopy, ultra violet-visible (UV-Vis) spectroscopy and grazing incidence X-ray diffraction (GI-XRD). The FESEM images clearly showed agglomerated TiO₂ particles on the surface of the stainless steel, while EDX results further confirmed the presence of TiO₂. The photocatalytic antibacterial activity of the synthesized TiO₂ photocatalysts on stainless steels were then tested out by using Escherichia Coli (*E.Coli*) in agar plates at 37 °C for 24 h.

Keywords: Titania, photocatalysts, automatic film applicator, coatings, physicochemical properties, photocatalytic activity

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1. INTRODUCTION

Titania (TiO₂) is the most commonly used photocatalyst in various reactions due to its redox properties, chemical stability, low toxicity, biocompatibility and cost effectiveness [1]. Among the most well-known uses of titania are in purification of water and air, solar power systems, lithium batteries, self-cleaning and antifogging surfaces, deodorant manufacture, selective synthesis of organic compounds and photocatalytic pathogen antibacterial [2-4]. Two conditions are necessary to have good photocatalytic system, which are the need for high surface area and the TiO₂ must be in anatase form while being easily accessible to the photons [5]. It has been suggested that TiO₂ in anatase-form is more active than the rutile phase [6]. The reactivity of these two phases can be differentiated by bulk transport of excitons to the surface. A previous research utilized high-quality epitaxial TiO₂ films of the two polymorphs, evaluating the photocatalytic activity as a function of TiO₂-film thickness [7]. For anatase, the activity increased for films up to ~5 nm thick, while the rutile films reach their maximum activity at the thickness of only

~2.5 nm. This shows that charge carriers excited deeper in the bulk for anatase, which contribute to the surface reactions, as compared to the rutile phase.

One of many usage of TiO₂ as a photocatalyst is in inhibiting bacterial growth [8, 9]. Previously, titania has been reported to have antibacterial and anti-adhesion properties of microorganisms due to the photogenerated reactive oxidant species. The hydroxyl radicals and superoxide can completely degrade most of the organic pollutants, bacteria fungus and even viruses from water. TiO₂ is generally coated onto the surface of a substrate material and the material's photocatalytic antibacterial activity is then investigated.

Among all the substrates that have been used, stainless steels are believed to be one of the most susceptible materials for bacterial adhesion [10]. Some of the researches that have been carried out utilized chemical vapour deposition (CVD), sputtering, sol-gel method, spray pyrolysis and liquid-phase deposition to deposit a TiO₂ film layer on the substrate materials, including stainless steels [11]. However, these methods involve multiple steps and require a very long processing time. In addition, previous

methods have also showed incompatibility with the selected substrate material, which sometimes caused the active material's surfaces to be prone to cracking or pulverization due to mechanical strain [12].

In this study, TiO₂-based photocatalysts have been coated on the surface of stainless steels by using an automatic film applicator. Apart from TiO₂, a small amount of polyvinyl alcohol and stabilizer have been mixed together to enhance the adhesion with the substrate. The photocatalytic antibacterial activity of the stainless steels coated by TiO₂-based photocatalysts was then tested out by using *Escherichia Coli* (*E. Coli*) in agar plates at 37 °C for 24 h.

2. EXPERIMENTS

2.1 Chemical and materials

The raw materials used in this study were commercially obtained pure TiO₂ (JRC-TIO-01) powder provided by Ishihara Sangyo Kaisha, Ltd, Japan. Other chemicals used in the coating process were polyvinyl alcohol (PVA) (Sigma-Aldrich, 99%) as the binder, ammonium citrate tribasic (Sigma-Aldrich, 97%) as the dispersant and distilled water as the solvent. Apart from that, acetone and ethanol were used as the cleaning solvents.

For the photocatalytic testing, the raw material used were glucose, ammonium chloride (NH₄Cl), magnesium sulphate heptahydrate (MgSO₄.7H₂O, Sigma-Aldrich, ≥98%), iron (III) chloride hexahydrate (FeCl₃.6H₂O, Sigma-Aldrich, 97%) and agar. Distilled water was used as the solvent.

2.2 The Coating Process

Plates of stainless steels have been used as the substrate material in this research. The substrates were first cut into pieces in the dimensions of 30 mm × 50 mm. The substrates were then washed with acetone for 15 min using an ultrasonic cleaner by immersing them into a beaker containing acetone so as to remove dirt and any other contaminants. Following that, the substrates were washed again with ethanol, before being ready for the coating process.

The TiO₂ powder together with the 0.54 g of polyvinyl alcohol and 0.05g of ammonium citrate tribasic were mixed inside the ball milling jar containing the 9.13 g of solvent (distilled water), after which they were ball-milled for 3 h in the presence of 2 balls of 5 mm diameter zirconia balls using the ratio of balls to powder of 10:1. The amounts of TiO₂ powder used were 0.10 g, 0.50 g, 1.00 g and 2.00 g for each coating mixtures.

An automatic film applicator was used for coating the stainless steels substrate with the photocatalytic mixture of TiO₂, following the method described by Abbas *et al.* [13], but with some modifications. The machine was equipped with wire-wound bars with very small gaps of 150 μm,

which was based on the required coating thickness. The automatic film applicator was then switched-on from the main supply. The substrate was placed directly under the wire-wound bar and the whole set up was adjusted until when there was a grip between the substrate and the wire-wound bar material. An amount of the prepared coating material was then poured on to the substrate and at a draw-down speed of 50 mm/s the wire-wound across the entire surface of the substrate and as a result it provided a smooth and uniform coating on the substrate due to the good control of the shear rate of the wire-wound bar during coating. The slurry compositions of the TiO₂ film coated onto the substrates were 0.1 g, 0.5 g, 1.0 g and 2.0 g respectively. The coated samples were then allowed to dry under atmospheric condition for 24 h. After that, it was further dried in an oven at a temperature of 100 °C for 1 h before proceeding to the final heating stage. A few testing on heating temperature has been carried out which were 600 °C, 400 °C, 300 °C and 200 °C to identify the effective coating on the substrate. The best heating temperature was then selected. The samples were effectively heated at 200 °C for 1 h to ensure affecting the coating of TiO₂ on the surface of stainless steels.

2.3 Characterization of samples

The prepared coated samples were characterized using various instruments. A Crossbeam 340 FIB-SEM from ZEISS was used to identify the properties of the photocatalysts that can be extracted from the microscopic feature of micrographs. Besides that, the elemental composition was determined by employing energy dispersive X-ray analysis (EDX) by X-Max Oxford instrument. The spectrum from the EDX will display several peaks that are unique for the respective atom, thus corresponding to a single element. X-ray diffraction (XRD) model Rigaku Smart Lab from Germany was used to record diffraction monochromatic pattern of the prepared samples in the 2θ range of 20° – 80°. For the determination of bonding types, ATR-FTIR was performed using a Frontier FTIR spectrometer. The spectra were recorded in the range of 650 to 4000 cm⁻¹. A LAMBDA 33 UV/Vis diffuse reflectance spectrophotometer was used to measure the band gap energy produced by the coatings of TiO₂.

2.4 Photocatalytic Testing

The photocatalytic activities of the prepared samples were testing towards *Escherichia Coli* (*E. Coli*). The testing, known as inhibition test, was conducted in a Laminar flow cabinet model ESCO. The agar medium was prepared by mixing 0.25 g of glucose, 0.5 g of ammonium chloride (NH₄Cl), 0.1 g of magnesium sulphate heptahydrate (MgSO₄.7H₂O), 0.0025 g of iron (III) chloride hexahydrate (FeCl₃.6H₂O) and 10 g of agar, into a 500 mL Schott bottle. All the components above were dissolved in 400 mL of distilled water. The pH of the medium solution was adjusted to 7.0 with either sodium hydroxide (NaOH) or hydrochloric

acid (HCl). The volume was then added until 500 mL with distilled water. 250 mL of the medium was dispensed into two 250 mL Schott bottles and both of bottles then underwent autoclave process. After each of the prepared medium has been sterilized and allowed to cool till 50 °C, the medium was slowly poured into petri plates (20 mL/plate).

The technique used to spread the bacterial growth is called Streak Plate Technique. A loop was flamed and allowed to cool afterwards. A small amount of one culture (*E.Coli*) on the loop was taken and concentrated in a small area at the edge of the plate. The loop was sterilized after finishing each cross-streak. Then, the plates involved were incubated and cultured for overnight at constant temperature of 37 °C before the test. Once the pure culture of *E.Coli* has been established, the coated stainless steels were placed on the nutrient agar's surface in triplicate. The petri plates were then incubated under the temperature of 37 °C for 24 h.

3. RESULTS AND DISCUSSION

3.1 Morphology and composition by FESEM and EDX analyses

Figure 1 revealed the morphology of all the TiO₂-based photocatalysts samples obtained from the FESEM analysis. All scanning were made with magnification of 50 000 times and 7.0 kV of scanning voltage. From the images, it can be seen that the TiO₂ in the samples are somewhat spherical in shape with the size range of 1.0 – 10.0 μm. Most of the TiO₂ particles can be seen agglomerated on the surface of the stainless steel.

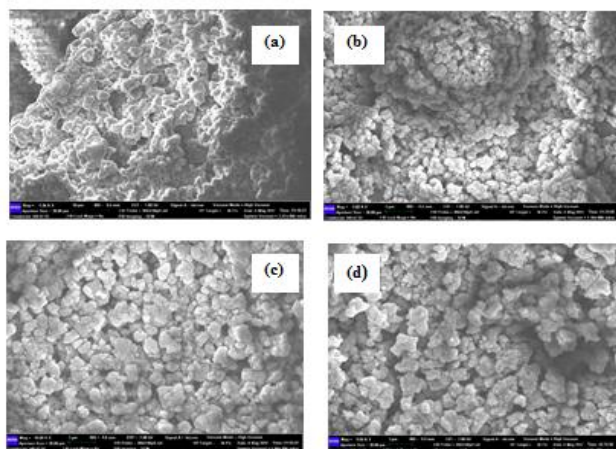


Fig. 1 FESEM images of (a) 0.10 g of TiO₂, (b) 0.50 g of TiO₂, (c) 1.0 g of TiO₂, and (d) 4.14 g TiO₂ on stainless steel plates.

EDX analysis was carried out in order to study the distribution of the elements present on the surface of the TiO₂ photocatalysts. From the analysis obtained shown in Figure 2, the coated samples consist of titanium (Ti), oxygen (O) and carbon (C). No other element can be observed except for the impurity peaks from the coating substrate. The

impurity peaks might also be due to the presence of platinum on the surface of the samples. All the photocatalysts showed a substantial amount of Ti.

Table 1 shows the atomic composition of elements present in the material coated on the surface of stainless steels with different amounts of TiO₂ and final heating temperature of 200 °C. All of the samples show the highest percentage of Ti species compare to O and C elements. Although EDX analysis can be extremely useful, it only analyze the area that is scanned and does not represent the whole sample. In Sample A, a high percentage of C (36.4%) was measured. This might be due to the low amount of TiO₂ used (only 0.10 g).

Table 1 The atomic composition of elements present in the material coatings on the surface of stainless steels with different amounts of TiO₂ after heating at the temperature of 200 °C

Photocatalysts	Atomic Ratio (%)		
	Ti	O	C
Sample A with 0.10 g of TiO ₂	37.9	25.8	36.4
Sample B with 1.00 g of TiO ₂	64.2	32.5	3.3
Sample C with 2.00 g of TiO ₂	50.4	47.6	2.1
Sample D with 4.14 g of TiO ₂	50.1	46.9	3.1

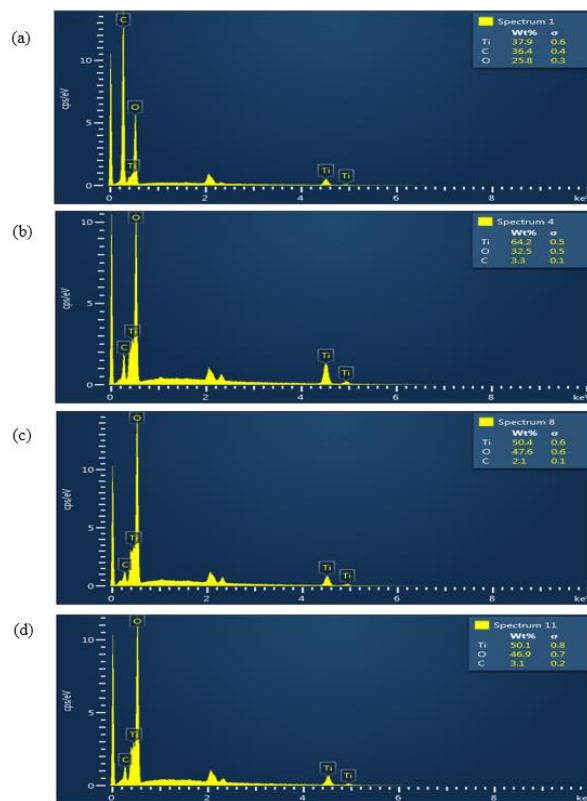


Fig. 2 EDX spectra of (a) 0.10 g of TiO₂, (b) 0.50 g of TiO₂, (c) 1.0 g of TiO₂, and (d) 4.14 g TiO₂ on stainless steel plates.

3.2 Crystallinity by XRD

The crystallinity and phase of the samples were determined by powder and GI-XRD. Figure 3 illustrates the XRD patterns of the commercial TiO₂ powder (Fig. 3 (a)) and sample of 2.00 g of TiO₂ coated on the surface of stainless steel (Fig. 3 (b)), which have been heated at the

temperature of 200 °C. The XRD pattern of the TiO₂ commercial powder confirmed the existence of anatase phase (PDF 01-075-2547) with the presence of sharp diffraction peaks located at $2\theta = 25.26^\circ$, 37.02° , 37.67° , 47.98° , 53.87° , 55.00° and 62.70° , which corresponded to (101), (004), (200), (105), (211), and (204), respectively. Meanwhile, the XRD pattern of TiO₂ solid also verified the formation of anatase phase (PDF 01-070-7348) with the presence of sharp diffraction peaks located at $2\theta = 37.91^\circ$, 47.96° , 53.93° , 55.04° , 62.69° , 70.17° and 74.98° , which corresponded to (101), (004), (200), (105), (211), and (204), although with decrease intensity.

The XRD pattern of TiO₂ commercial powder shows a peak at $2\theta = 25.26^\circ$ corresponding to the (101) reflection of anatase TiO₂. No other phase of rutile or brookite TiO₂ was observed. The same pattern has been observed for TiO₂ coated on the surface of stainless steel, which shows the characteristic anatase peak at $2\theta = 37.91^\circ$. However, the intensity of the peaks for coated TiO₂ is much lower than those of commercial TiO₂ powder. This might be due to the low amount of TiO₂ and the presence of other materials (substrate, binder, dispersant).

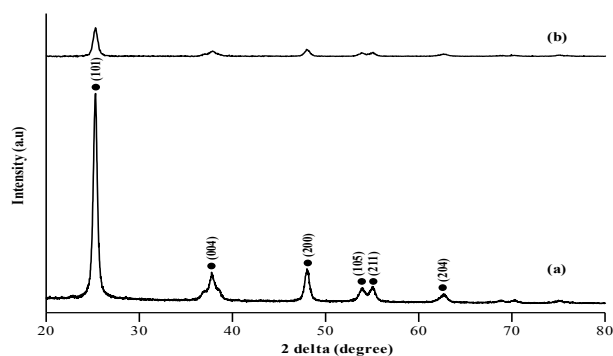


Fig. 3 XRD patterns of the (a) commercial TiO₂ powder and (b) 2.00 g of TiO₂ coated on the surface of stainless steels.

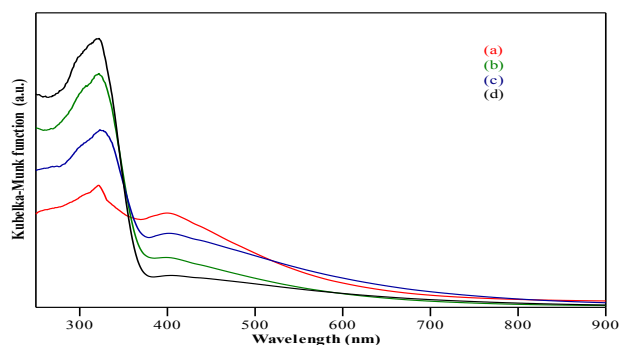


Fig. 4 UV-Vis diffuse reflectance spectra of photocatalysts with (a) 0.10 g of TiO₂, (b) 0.50 g of TiO₂, (c) 1.00 g of TiO₂, and (d) 2.00 g of TiO₂

3.3 Band gap energy by Ultraviolet Visible (UV-Vis) spectroscopy

The diffuse reflectance UV-Vis spectra of the samples expressed in terms of Kubelka-Munk function are presented in Figure 4. Based on spectra, there was one major

peak at around 320 nm for all of the prepared TiO₂ photocatalysts. The absorption peak of TiO₂ at around 320 nm is linked to the creation of octahedral of polymeric Ti species, which has been reported previously [14]. The other samples of TiO₂ also exhibited absorption peak at around 320 nm, although different amounts of TiO₂ were used.

Based on the UV-Vis absorption spectra, the effect of TiO₂'s amount on the band gap energy (E_g) of the TiO₂ composites was then studied. The E_g can be determined from Tauc plot by plotting $(\alpha h\nu)^{2/n}$ versus $h\nu$. It has been reported that TiO₂ with anatase phase prefers indirect transition, implying that n value should be 4 [15]. The E_g of the TiO₂ photocatalysts synthesized was estimated based on the value of x -intercept by taking the linear extrapolation in the plot of $(\alpha h\nu)^{2/n}$ versus $h\nu$, as shown in Figure 5.

From the Tauc plots, the indirect band gap energies of the commercial TiO₂ photocatalysts are estimated to be 3.22, 3.32, 3.18 and 3.37 eV, respectively. It has been reported that particles with higher surface area have lower band gap energy as compared with the same particles with smaller surface area. Based on the results showed, sample C with 1.00 g of TiO₂ exhibited band gap energy slightly lower than sample A with 0.10 g of TiO₂. This might be due to the TiO₂ being dispersed on the surface of the substrate.

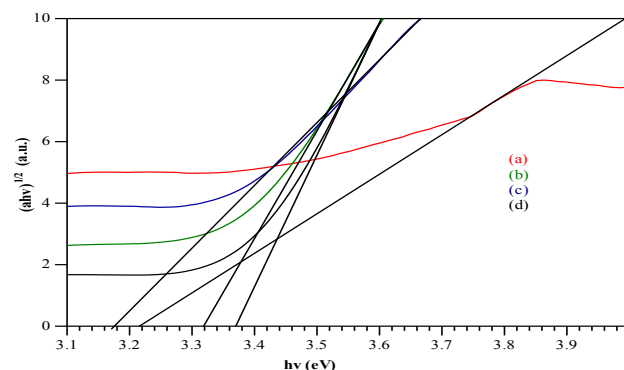


Fig. 5 Tauc plots of the samples with (a) 0.10 g of TiO₂, (b) 0.50 g of TiO₂, (c) 1.00 g of TiO₂, and (d) 2.00 g of TiO₂.

3.4 Functional Groups by FTIR Spectroscopy

Figure 6 shows the FTIR spectra of the TiO₂ photocatalysts samples coated on the surface of stainless steels with different amounts of TiO₂. All of the spectra show a band at 3293.06 cm^{-1} which corresponded to the stretching vibration of hydroxyl groups. Another peak observed in the spectra at 1984.6 cm^{-1} corresponded to the bending mode of the hydroxyl groups. These hydroxyl groups and adsorbed water are usually present on the surface of the TiO₂. The characteristic vibration of the inorganic Ti-O stretch was also observed in the range of $650\text{ to }690\text{ cm}^{-1}$.

3.5 Photocatalytic Activity

The photocatalytic activity of TiO₂ photocatalysts coated on the surface of stainless steels was carried out by inhibition test. In the inhibition test, *Escherichia coli*

(*E.Coli*) bacteria were used and carried out in agar plates at 37 °C for 24 h. The preparation methods were done according to the method by Sanders [16]. However, in this study, regrettably, the coated TiO₂ photocatalysts on stainless steels did not show any antibacterial activity towards the *E.Coli* species. After 24 h, the bacteria can be seen growing all around the agar, with no inhibition effect at all. This might be caused by a few reasons. One of the most possible reason might be due to the small amount of TiO₂ used. As other materials were also present in the samples, the photocatalytic active surface of the TiO₂ might had been covered.

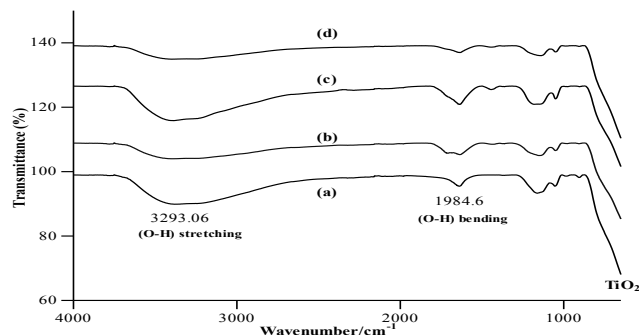


Fig. 6 FTIR spectra of TiO₂ photocatalysts coated on stainless steels with different amounts of TiO₂; (a) 0.10 g of TiO₂, (b) 0.50 g of TiO₂, (c) 1.00 g of TiO₂, and (d) 2.00 g of TiO₂.

Apart from that, it has also been reported that the presence of other metals, such as silver (Ag), is needed in order to induce antibacterial activities in TiO₂ samples [17]. As the samples prepared in this work did not include the addition of other metals, the photocatalytic antibacterial activity might not have been induced.

In some cases, Liu *et al.* had reported that the unmodified titania has lower tendency in inhibiting the growth of Escherichia coli and other bacteria species [17] [18]. Therefore, the probability for unmodified titania to inhibit the growth of bacteria is lower. Figure 7 shows the inhibition test for titania photocatalysts samples with different compositions. As can be seen clearly, even in the presence of the TiO₂ coated on stainless steels samples, the bacteria still continue to grow around the agar.

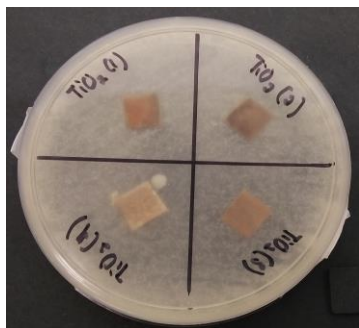


Fig. 7 Inhibition test for TiO₂ coated on stainless steels samples.

4. CONCLUSION

Experimental results showed that titania-based photocatalysts can be effectively functionalized on stainless steels by using the automatic film applicator method. The physicochemical properties of the titania-based photocatalysts have been successfully determined by using FESEM-EDX, XRD, UV-Vis and FTIR spectroscopies. Characterization by using FESEM showed that the titania particles coated on the surface of stainless steels consists of almost spherical particles agglomerated on the surface of the substrate. Meanwhile, the EDX confirmed the presence of Ti element in the coated materials. Furthermore, the anatase crystallinity of the titania has been proven by the XRD diffraction pattern. Additionally, the UV-Vis spectroscopy identified the band gap energy of titania photocatalysts at a range of 312 to 340 eV and FTIR spectroscopy displayed the stretching bands for the functional groups of titania in the range of 650 to 690 cm⁻¹.

When the photocatalytic activity of TiO₂ photocatalysts coated on the surface of stainless steel was carried out by inhibition test of *E.Coli* bacteria, unfortunately, the coated TiO₂ photocatalysts on stainless steel did not show any antibacterial activity. After 24 h, the bacteria can be seen growing all around the agar, with no inhibition effect at all. This might be caused by the small amount of TiO₂ used. As other materials were also present in the samples, the photocatalytic active surface of the TiO₂ might had been covered. Apart from that, as the samples prepared in this work did not include the addition of other metals, the photocatalytic antibacterial activity might not have been induced.

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