Synthesis TiO$_2$-Ag thin film by DC Sputtering method for dye degradation

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Abstract. Titanium dioxide (TiO$_2$) is well known as the most active and stable semiconductor as an environmentally friendly photocatalytic material to degrade pollutants in aqueous and gas. In this research, TiO$_2$ thin film was synthesized on a stainless steel surface using DC sputtering method. To enhance the photocatalytic activity, the TiO$_2$ thin film was doped with a silver (Ag) also using DC sputtering method. The surface morphology, chemical composition, and crystal structure of the thin film were characterized using scanning electron microscopy –energy dispersive spectroscopy (SEM-EDX) and X-rays diffraction (XRD), respectively. Based on SEM-EDX analysis, it’s found that the content of silver (Ag) is 10.5 % weight or 2.56 % at. This condition was achieved for 2 minutes of deposition time. The photocatalytic activity of TiO$_2$ and TiO$_2$-Ag thin film was studied using UV light and sunlight. As a model pollutant, it’s used methylene blue. It’s found that, if the film exposure using UV light, the absorbance for TiO$_2$ film is 35.85 % and 64.26 % for TiO$_2$-Ag thin film. If the film exposure using sunlight, the absorbance for TiO$_2$ film is 17.5 % and 76.74 % for TiO$_2$-Ag thin film. It can be concluded that the effect of Ag doping can enhance the photocatalytic activity of the thin film.

1. Introduction

Semiconductor materials in recent years have been a concern, especially in their contribution to the field of photocatalysts for processing organic waste [1]. Titanium dioxide semiconductor materials have been extensively studied as photocatalyst semiconductors due to its physical and chemical stability, insoluble in water, inexpensive, non-toxic, biocompatible, etc [2]. The process of the waste photocatalyst is waste treatment, with semiconductor nanomaterial rocks as catalysts and with the help of light waves so that organic waste will be oxidized to H$_2$O and CO$_2$ [1].

Many methods used to synthesize TiO$_2$ include thermal, oxidation, electron beam evaporation, chemical vapor deposition, sol-gel, and sputtering [3]. Direct Current (DC) sputtering is a good method for making thin layers on a substrate by breaking bonds between atoms on the target so that atoms will be arranged on the substrate and form a new thin layer [4]. Some of the advantages of DC sputtering are it can produce a thin layer of material which has a high melting point (melting point TiO$_2$ = 1853 °C), can deposit solid materials, able to save material from being deposited, has strong adhesion, the thickness of the layer can be accurately controlled, cheap operations, can do multiple layers of deposition, the adhesion force between the film and the surface of the substrate is stronger.

Titanium dioxide, which is most often used in photocatalysts, is in the form of anatase because it’s surface area is better than the form of rutile and brookite crystals [5], and the band-gap energy possessed is 3.2 eV [2].
However, TiO₂ can only be excited under UV light with a wavelength of less than 400 nm [6]. A TiO₂ surface modification process is needed to improve the performance of TiO₂. The modification process is done by the doping process. The doping process of titanium nanoparticles is usually carried out with metals such as Au, Ag, Cu, Bi, Pt, and others [7]. The use of metal as a dopant aims to add electrons to TiO₂ so that TiO₂ can work in visible light.

The use of Ag metal as a dopant has a significant effect on the performance of TiO₂ because Ag is a metal that has the highest conductivity among other metals, high catalytic activity, good optical properties, anti-microbial and relatively inexpensive compared to other precious metals [8]. The presence of small Ag nanoclusters on TiO₂ increases the photocatalytic activity under both UV and visible light irradiation [9]. Ag-modified TiO₂ photocatalysts also enhanced the antimicrobial properties, which has the possibility of a wide range of applications for the decomposition of pollutants and environmental purifications [10].

In this study, it was reported that TiO₂ and TiO₂-Ag thin films would be used as photocatalyst materials. Things reported include making thin TiO₂ and TiO₂ coatings using the DC sputtering method, characterizing the thin film produced, and the degradation results of methylene blue using TiO₂ and TiO₂-Ag.

This study is useful to obtain information on the process of making TiO₂ and TiO₂ thin films doped by Ag metal using the DC Sputtering method. Also, this research can complement other studies regarding the manufacture of TiO₂ and its modification in use as photocatalytic material. The research results are expected to be applied in solving the waste problem.

2. Experimental

2.1. TiO₂ Thin Film Synthesis

The making of TiO₂ thin films with DC Sputtering was carried out at the PSTA-BATAN Particle Physics Laboratory. The titanium target used has a purity of 99.99%, a thickness of 3 mm, and a diameter of 60 mm, while the stainless steel substrate used has a measurement of 1 x 2 cm. Before the sputtering process, the specimens were grounded and polished to produce a smooth and flat specimen. The grinding process is carried out using abrasive paper and polished mechanically with autosol. The polished specimens were washed with 70% alcohol for 15 minutes in an ultrasonic cleaner machine and dried at room temperature. The sputtering process begins with a vacuum forming with a rotary vacuum reaching a pressure of 4x10⁻³ torr and followed by vacuum diffusion, reaching a pressure of 4x10⁻⁴ torr.

The gas used in the sputtering process is Ar and O₂ gas, with a ratio of 70/30. The Sputtering process is carried out with time variations of 0.5 hours; 1 hour; 1.5 hours; 2 hours; and 3 hours with a voltage given 4 kV with a current of 10 mA for obtaining the optimal length of time from TiO₂ synthesis.

2.2. Doping Ag

After obtaining the optimal length of time from TiO₂ synthesis, which is 1.5 hours, the process is continued with Ag metal doping, which was carried out by replacing the Ti target into the Ag target (purity of 99.99%). Furthermore, the sputtering process was carried out, beginning with a vacuum forming using a rotary vacuum, reaching a pressure of 4x10⁻³ torr, and continued with diffusion vacuum reaching a pressure of 4x10⁻⁴ torr. The gas used in the sputtering process is Ar gas with time variations of 0.5 minutes, 2 minutes, 3 minutes, 4 minutes, and 5 minutes.

After TiO₂-Ag thin film was formed, then calcination was carried out at a temperature of 450°C for 3 hours to form an anatase phase which has good photocatalyst properties.

2.3. Characterization

The characterization was carried out in the form of photocatalytic test, X-Ray Diffraction testing, SEM testing, and UV-Vis testing.

2.3.1. Photocatalytic test
The parameters of the photocatalytic test in this study will be limited only to the target pollutant concentration and lighting time, while the other parameter variables are considered constant. Commonly, research on the degradation of pollutants uses a quite low pollutant target concentrations (only a few ppm). This activity aims to simplify the level of the reaction process that occurs and facilitate researchers in observing the results.

While for lighting, time is only limited to 20 minutes because the optimal absorption of light that affects the process of pollutant degradation is between 0 to 20 minutes [11].

Methylene blue with a concentration of 2 ppm was used to test the degradation of synthesized TiO$_2$ and synthesized TiO$_2$-Ag. The synthesized thin film was put into methylene blue solution for 20 minutes, which was carried out on UV light and sunlight alternately. Then the absorbance was measured using a UV-Vis spectrophotometer for methylene blue, before and after the degradation process.

2.3.2. X-Ray Diffraction
TiO$_2$ thin film sample was characterized using XRD analysis at the ITS laboratory, Surabaya. XRD testing was carried out to obtain information relating to the crystalline structure of the synthesis results.

2.3.3. SEM
TiO$_2$ thin film sample was characterized using SEM analysis at the ITS Mechanical Engineering Laboratory, Surabaya. SEM testing is carried out on specimens that have the optimum length of time from TiO$_2$ synthesis. SEM testing was carried out to determine the thickness of the TiN layer.

2.3.4. UV-Vis
TiO$_2$ thin films and TiO$_2$-Ag synthesized immersed in methylene blue dyes with a concentration of 2 ppm for 20 minutes, then absorbance values were calculated before and after degradation.

3. Discussion

3.1. TiO$_2$ plate synthesis
In this study, TiO$_2$ nanoparticles were obtained by DC Sputtering technique, which is the technique of making thin layers using Ti targets on stainless steel substrates with the principle of breaking bonds between atoms on the target so as to produce TiO$_2$ plate nanoparticles morphologically, which will be used as photocatalysts for substance degradation methylene blue color.

TiO$_2$ plate synthesis is the first step of this research with a variation of 0.5 hour deposition time; 1 hour; 1.5 hours; 2 hours; and 3 hours. The difference in the duration of deposition time affects the amount of TiO$_2$ attached to the substrate, the longer the deposition time, the more TiO$_2$ attached will be, which in this study was observed by visual observations shown in Figure 1. For each plate with different time deposition, different colors are obtained at the time of 0.5 hours, obtained in light blue, at 1-hour purplish-blue, at 1.5 hours gold, violet, and greenish-yellow at 2 and 3 hours. The color difference is caused by differences in thickness on each plate [12].

This step is carried out to find the optimum thickness of TiO$_2$ thin films. Its thickness strongly influences the TiO$_2$ thin films’ hemispherical reflectance. At its optimum thickness, the maximum peak intensities of TiO$_2$ thin films show around 32% spectral reflectance in the visible wavelength range of 380-780 nm [12], which is corresponded to gold color in the visible spectrum at this research.

![Figure 1. TiO$_2$ Plate Synthesis Results (a) 0.5 hour, (b) 1 hour, (c) 1.5 hour, (d) 2 hour, (e) 3 hour](image-url)
Characterization using SEM was performed on samples with the optimal length of time from TiO\(_2\) synthesis, which is 1.5 hours. The morphology of TiO\(_2\) is shown in Figure 2. Based on Figure 2, it can be seen that the morphology of TiO\(_2\) shows the formation of nanoparticle structures. These TiO\(_2\) nanoparticles were obtained when the nanoparticles were released from the Ti plate and bind to the O\(_2\) gas then transformed into nanoparticles. The size of the nanoparticles obtained has relatively the same size.

Figure 3 shows the results of SEM to measure the cross-section; it can be seen that the thickness of the synthesized TiO\(_2\) with a length of DC sputtering for 1.5 hours is around 1.72 \(\mu\)m. However, there are differences in the height of TiO\(_2\) in the sample; and this is probably due to the inhomogeneity of the stainless steel substrate when doing polish.

![Figure 2. Morphology of 1.5 hours TiO\(_2\) Synthesis](image)

![Figure 3. Cross-section of 1.5 hours TiO\(_2\) Synthesis](image)

3.2. Modification of Ag with Sputtering Method
The next stage after the TiO\(_2\) optimization results are obtained, it is modified with Ag metal. Ag modification was carried out to increase the photocatalytic activity of TiO\(_2\). Ag modification is done by the sputtering method with a variation of 0.5 minutes; 2 minutes; 3 minutes; 4 minutes; and 5 minutes deposition time.

Ag doping results on TiO\(_2\) thin films can be observed based on the effect of reaction with oxygen. The deposition is said to be optimal if the reaction of TiO\(_2\) with oxygen occurs evenly on the physical thin film during the deposition process so that the physical of TiO\(_2\) becomes porous homogenously [12].
Another thing that can be observed visually from TiO₂ deposition with Ag is its chromaticity character. During the deposition process, it also gradually changes the appearance of its colors. The colors change diagram is elliptical, with the peak area, which is the optimal condition. The longer the process lasts after the peak is passed, the color will change closer to the color character as at the beginning of the process [13].

In the visual observation of Ag deposition results on TiO₂, there is a color change shown in Figure 4. Figure 4 shows that the longer the deposition time is carried out, the plate surface will be white. Figure 4 (a) shows that at the time of initial deposition, the experimental plate was pale yellow. Then it becomes more even and thicker in yellow at 0.5 minutes and 2 minutes, as in Figure 4 (b) and 4 (c). After 2 minutes have passed, which is at minute 3, the plates slowly turn pale again, as in Figure 4 (d). Figure 4 (e) the 4th minute and Figure 4 (f) the 5th minute show the development of increasingly white color changes after passing the peak period, approaching the pale yellow character, that is, as at the beginning of the experiment. So it can be decided that the optimum Ag deposition condition is at 2 minutes.

![Figure 4. Synthesized plates (a) TiO₂, TiO₂ deposited in Ag (b) 0.5 minutes; (c) 2 minutes; (d) 3 minutes; (e) 4 minutes; (f) 5 minutes](image)

Analysis of TiO₂-Ag was tested by X-Ray Diffractometer to obtain information relating to the crystalline structure of the synthesis results. In this characterization, the samples tested were samples prepared from the synthesis results of TiO₂-Ag with Ag deposition time for 2 minutes. The diffractogram of TiO₂-Ag and the diffractogram of 316L stainless steel substrate are shown in Figure 5. Figure 5 (a) is the X-ray diffractogram pattern of the TiO₂-Ag plate synthesized, as shown by the peaks which provide information on the identity of the synthesized TiO₂-Ag crystalline phase. Based on Figure 5 (a) shows the peak spectrum of 316L stainless steel is more dominant than TiO₂-Ag. In Figure 5 (a), there is a peak of rutile TiO₂ at an angle of 2θ around 27, but the Ag spectrum does not seem likely due to the Ag spectrum covered by a stainless steel spectrum.

![Figure 5. Diffractogram of TiO₂-Ag and 316L stainless steel substrate](image)
The crystal size of TiO$_2$ is calculated by the Scherrer equation. From the calculations, the resulting crystal size of TiO$_2$ is 1.87 nm. Characterization with SEM was carried out on TiO$_2$-Ag samples with the optimum deposition time for 2 minutes. The morphology of Ag analyzed using SEM is shown in Figure 6. The synthesized EDS spectrum of TiO$_2$-Ag is shown in Figure 7. From Figure 6, it can be seen that TiO$_2$-Ag has a relatively uniform morphology.

**Figure 5.** XRD test result (a) TiO$_2$-Ag Diffractogram, (b) 316L stainless steel substrate Diffractogram [14]

Figure 7 shows the EDS results of synthesized TiO$_2$-Ag with 2 minutes of Ag deposition. EDS is a technique used to analyze components in materials under SEM. This method detects X-rays produced as a result of electron beam interactions with samples. With this method, the mapping of the distribution of chemical elements in the material can be obtained. Based on the spectrum, the average weight ratio (% wt) of Ti, O, and Ag is 14.21%, 13.66%, and 3.27%, while the ratio of the number of atoms (% At) Ti, O, and Ag is 12.04%, 34.66%, and 1.23%. In the spectrum, there are other elements such as Ni, Cr, Fe, Mo, P, Si, and Al, which are 316L stainless steel constituents. Table 1 shows the weight percent (weight %) and atomic percent (% At) of Ti, O, and Ag, on their sums, respectively. The results of the EDS mapping of the distribution of Ti, O, and Ag are shown in Figure 8.

**Figure 6.** The morphology of 2 minutes Ag deposition analyzed using SEM (a) 10,000x (b) 20,000x

**Figure 7.** EDS results of synthesized TiO$_2$-Ag with 2 minutes of Ag deposition.
Figure 7. EDS results of synthesized TiO₂-Ag with 2 minutes Ag deposition

Table 1. Percent weight (% wt) and atomic percent (% At) Ti, O, and Ag elements of the amount of Ti, O, and Ag

| Element | %wt | %At  |
|---------|-----|------|
| Ti      | 45.63 % | 25.11 % |
| O       | 43.86 % | 72.31 % |
| Ag      | 10.5 %  | 2.56 %  |

Figure 8. EDS Mapping Area of TiO₂-Ag with 2 minutes Ag deposition (a) Ti, (b) O, and (c) Ag

Based on the results of the EDS mapping, it can be seen that the distribution of Ti, O, and Ag is quite even on the plate. In the Ag area mapping, there are some of Ag particles which accumulate with each other because when the Ag ion splashes towards the thin film TiO₂, the direction of the spark is in all directions and is irregular.

3.3. Photocatalytic Test

Photocatalytic tests were carried out to prove the improvement of the synthesis properties of TiO₂ compared to TiO₂-Ag using 2 ppm methylene blue. Methylene blue is one of the dyes that are widely used in the industry. The use of dyes has been widely used as samples for photocatalytic tests because dyes are difficult to degrade using conventional methods, and measurement of their concentration is easily determined by measuring the absorbance [11].

Figure 9 shows the percentage of degradation for 10 and 20 minutes with TiO₂ plates, where the highest percentage of degradation occurred on TiO₂ plates with a sputtering time of 1.5 hours. In the study of Malengreaux et al. 2012 [13], the results of 24-hour methylene blue degradation with TiO₂ produced from the most optimum sol-gel method at a thickness of 80 nm with 93% degradation.

Figure 10 shows the highest percentage of degradation results at 20 minutes of degradation time so that the degradation was not carried out for a longer time due to the lack of information on the stability of sputtering TiO₂ thin films. During the first 30 minutes in the darkroom, in the dark conditions, there
is no light source so that it cannot produce hydroxyl radicals, therefore methylene blue experiences desorption adsorption events reported by Xu, Rangaiah, and Zhao, 2014 [11]. Percentage reduction in methylene blue concentration continues to increase up to around 15%. In this study, the process reached its maximum point at 20 minutes of degradation.

![Figure 9. Effect of sputtering time on % degradation](image)

![Figure 10. Relationship of % degradation and time of degradation](image)

### 3.3.1. Photocatalytic test in sunlight

The degradation process is carried out in the sun and under UV light to determine the effect of modification of Ag on the surface of the TiO₂ plate. Photocatalytic tests under sunlight were performed to determine the performance of TiO₂-Ag thin films, which can be seen from the percent degradation of methylene blue obtained so that the application of TiO₂-Ag plates can be used in the sun so that it is more economical. In this study, the photocatalytic test was carried out with sunlight intensity ranging from 790 lux.
Figure 11 shows the greatest degradation results obtained on TiO$_2$ plates deposited with Ag for 2 minutes. Based on SEM results in Figure 5 (c), Ag is evenly distributed with uniform size on the surface of TiO$_2$.

In the photocatalytic test under the sunlight, a comparison is made between percent degradation of TiO$_2$, percent degradation of TiO$_2$-Ag, and percent degradation of methylene blue without using a plate. Table 2 shows % degradation in the photocatalytic test under the sunlight.

Table 3 shows that the degradation of methylene blue with TiO$_2$ plates have better results compared to the degradation of methylene blue without plates. The photocatalytic test with TiO$_2$-Ag showed higher results than TiO$_2$ without deposition Ag. Based on the % degradation of methylene blue with the TiO$_2$-Ag plate, it was proved that the modification of Ag could improve the performance of the photocatalytic plate of the synthesized TiO$_2$. In the degradation of methylene blue in the sun, Ag will function as an electron donor to the TiO$_2$.

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**Table 2. Percent degradation in photocatalytic tests in the sun**

| Materials                        | % of degradation |
|----------------------------------|------------------|
| Methylene Blue                   | 1.01%            |
| Methylene Blue with TiO$_2$ catalyst | 17.5%        |
| Methylene Blue with TiO$_2$-Ag catalyst | 76.74%       |

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### 3.3.2. Photocatalytic test with UV light

The photocatalytic process carried out in UV light was obtained from the 10 W HIMAWARI lamp with three lights on the right side, three lights on the left, and three lights from above, which were 30 cm apart from the reactor. While the modified Ag dioxide was obtained from the sputtering of TiO$_2$ thin films with a time duration of 1.5 hours, which then continued with the DC sputtering process using the Ag target.

Figure 12 shows the largest degradation of methylene blue as much as 64.26% at Ag deposition time of 2 minutes, and decreased % degradation at 3 minutes deposition time. The longer the deposition time, the more deposited Ag will be. Excess Ag deposition can cover the surface of TiO$_2$, which will block photons from activating TiO$_2$. Therefore, the electron-hole formation will be inhibited and reduce % degradation.

In the photocatalytic test under UV light, a comparison of percent degradation was made. Between methylene blue using TiO$_2$ plates without modification, methylene blue using TiO$_2$-Ag plates, and methylene blue only. Table 3 shows the percent degradation of each plate.
The percentage of degradation on the TiO₂ plate was greater than that on methylene blue, but the percent degradation of the Ag modified TiO₂ plate was greater than the TiO₂ plate. In sunlight, the Ag metal deposited acts as an electron donor to the TiO₂ conduction band, which will produce oxidative material to degrade.

In UV light, Ag will act as a recombination inhibitor so that it will extend the life span of holes and electrons. Electrons tend to go to the valence band (to be stable), with Ag, the electrons will go to the Ag conduction band first, thus extending the life span of holes and electrons [15]. Therefore, the percent degradation of methylene blue on the TiO₂-Ag plate is greater than that of the TiO₂ plate.

Based on Figure 13, the degradation of methylene blue with TiO₂-Ag in the best UV light and sunlight in TiO₂ was carried out by sputtering with Ag for 2 minutes. In degradation with UV light percent degradation as much as 64.27%, while in sunlight percent degradation is 76.74%. The addition of excessive Ag deposition time will cover the surface of TiO₂ material, so the TiO₂ catalyst cannot interact with methylene blue. The absence of this interaction is indicated by a decrease in% degradation along with the length of time of deposition of Ag in UV light and sunlight.

The degradation of methylene blue with TiO₂-Ag in sunlight is better than in UV light because sunlight has a wider wavelength range than UV light. In sunlight, Ag, which has many-electron clouds, is activated by visible light so that many Ag electrons are transferred to the TiO₂ conduction band. Also, sunlight has a wavelength between 300 - 800 nm. In sunlight, it also contains 10% of UV light [15].
4. Conclusion

The study showed that it was possible to synthesized TiO$_2$-Ag thin film by DC Sputtering method. DC Sputtering method can do multiple layers of deposition that is evenly distributed on the entire surface. In this study, the TiO$_2$ thin film synthesis process with DC Sputtering was successfully carried out with an optimum duration time of 1.5 hours. While the process of modifying Ag nanoparticles on the surface of TiO$_2$ using the DC sputtering method was successfully carried out with an optimum Ag sputtering duration time of 2 minutes. TiO$_2$-Ag thin films have better photocatalytic activity in sunlight or UV light than sputtered TiO$_2$ thin films without modification of Ag. In degradation with TiO$_2$-Ag in UV light, degradation was 64.27%, whereas, in sunlight, it was 76.74%. Percent degradation with TiO$_2$ synthesized in UV light as much as 35.85% and in sunlight as much as 17.5%.

References

[1] R. Kralchevska, M. Milanova, M. Tsvetkov, D. Dimitrov, and D. Todorovsky, “Influence of gamma-irradiation on the photocatalytic activity of Degussa P25 TiO$_2$, “J. Mater. Sci., vol. 47, no. 12, pp. 4936–4945, 2012.

[2] Z. Hai, N. El Kolli, J. Chen, and H. Remita, “Radiolytic synthesis of Au-Cu bimetallic nanoparticles supported on TiO2: Application in photocatalysis,” New J. Chem., vol. 38, no. 11, pp. 5279–5286, 2014.

[3] M. Stamate, I. Vascan, I. Lazar, G. Lazar, I. Caraman, and M. Caraman, “Optical and surface properties TiO2 thin films deposited by DC magnetron sputtering method,” J. Optoelectron. Adv. Mater., vol. 7, no. 2, pp. 771–774, 2005.

[4] S. Widodo, “TEKNOLOGI PENDEPOSISIAN FILM TIPIS METAL DENGAN METODE DC-SPUTTERING,” 2012.

[5] M. Epifani et al., “Surface modification of TiO2 nanocrystals by WOx coating or wrapping: Solvothermal synthesis and enhanced surface chemistry,” ACS Appl. Mater. Interfaces, vol. 7, no. 12, pp. 6898–6908, 2015.

[6] A. L. Luna et al., “Synergetic effect of Ni and Au nanoparticles synthesized on titania particles for efficient photocatalytic hydrogen production,” Appl. Catal. B Environ., vol. 191, pp. 18–28, 2016.

[7] O. Tahiri Alaoui et al., “Elaboration, charge-carrier lifetimes and activity of Pd-TiO 2 photocatalysts obtained by gamma radiolysis,” J. Photochem. Photobiol. Chem., vol. 242, pp. 34–43, 2012.
[8] M. G. Méndez-Medrano et al., “Surface Modification of TiO2 with Ag Nanoparticles and CuO Nanoclusters for Application in Photocatalysis,” *J. Phys. Chem. C*, vol. 120, no. 9, pp. 5143–5154, 2016.

[9] E. Grabowska et al., “Modification of titanium(IV) dioxide with small silver nanoparticles: Application in photocatalysis,” *J. Phys. Chem. C*, vol. 117, no. 4, pp. 1955–1962, 2013.

[10] E. Kowalska et al., “Silver-modified titania with enhanced photocatalytic and antimicrobial properties under UV and visible light irradiation,” *Catal. Today*, vol. 252, pp. 136–142, 2015.

[11] X. Liu et al., “Photocatalytic and electrochemical degradation of methylene blue by titanium dioxide,” *Chin. Sci. Bull.*, vol. 59, no. 17, pp. 1964–1967, 2014.

[12] J. H. Lee, G. E. Jang, and Y. H. Jun, “Investigation and evaluation of structural color of TiO2 coating on stainless steel,” *Ceram. Int.*, vol. 38, no. SUPPL. 1, pp. S661–S664, 2012.

[13] C. M. Malengreau et al., “Optimized deposition of TiO2 thin films produced by a non-aqueous sol-gel method and quantification of their photocatalytic activity,” *Chem. Eng. J.*, vol. 195–196, pp. 347–358, 2012.

[14] R. Kartikasari and I. Aziz, “Corrosion Behavior of Plasma Nitrided SS316L Biomaterial Abstract:,” no. 1, pp. 29–37, 2017.

[15] Y. He, P. Basnet, S. E. H. Murph, and Y. Zhao, “Ag nanoparticle embedded TiO2 composite nanorod arrays fabricated by oblique angle deposition: Toward plasmonic photocatalysis,” *ACS Appl. Mater. Interfaces*, vol. 5, no. 22, pp. 11818–11827, 2013.