Photocatalytic Degradation of Acid Orange 7 by NiO-TiO$_2$/TiO$_2$ Bilayer Film Photo-Chargeable Catalysts

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Abstract: Photocatalysis as an eco-friendly technology has the potential to achieve the Sustainable Development Goals (SDGs). However, an improvement of conventional photocatalysts is necessary to overcome their limitations such as slow kinetics, wavelength for excitation, and environmental restrictions. In particular, the development of a photocatalyst that can operate even in the absence of light is constantly conducted, and a photo-chargeable photocatalyst could be one of the answers. In this paper, a heterojunction composed of TiO$_2$ and NiO-TiO$_2$ bilayer film photocatalyst (BLF) was prepared. The effect of the synthesis conditions of the NiO-TiO$_2$ layer on the photocatalytic properties was investigated. Photocatalytic degradation measurements were conducted with an acid orange 7 (AO7) solution under light and dark conditions. The highest degradation BLF was synthesized at a NiO loading of 52% and calcination temperature of 300 $^\circ$C. The prepared sample showed about five-fold greater photocatalytic activity of 48% in AO7 degradation after 8 h compared to an ordinary TiO$_2$ film (9%) under light conditions. Moreover, under dark conditions it exhibited 13.6% degradation, while the naked layers of TiO$_2$ and NiO-TiO$_2$ showed no degradation. The proposed mechanism suggested that photocatalysis in the dark was possible due to the stabilization of photogenerated holes by anionic intercalation during illumination.

Keywords: photocatalyst; titanium dioxide; nickel oxide; heterojunction; degradation

1. Introduction

TiO$_2$ is a well-known photocatalyst that has a wide band gap, and its electrons can be excited from the valence band to the conduction band when exposed to light with energy equal to the band gap [1]. Besides the photocatalytic activity, TiO$_2$ is environmentally friendly and abundant, not to mention that it is thermally, chemically, and biologically inert. Thus, TiO$_2$ has been applied in many fields, such as photolysis of water [2–4], CO$_2$ reduction [5], and organic molecules degradation [6–9]. In nature, TiO$_2$ exists in various phases, which are rutile, anatase, and brookite. However, anatase TiO$_2$ has proven to be the most active for photocatalysis [10]. Although TiO$_2$ is one of the fascinating photocatalysts, its photocatalytic activity is limited by its large band gap. Theoretically, the band gap of anatase or brookite TiO$_2$ is 3.2 eV, whilst that of rutile is at 3.0 eV [10]. Hence, TiO$_2$ needs energy under UV light ($\lambda < 400$ nm), which is a small proportion of solar energy. Moreover, the rapid recombination rate of photogenerated electrons and holes is also a problem. Hence the modifications to TiO$_2$ to improve its photocatalytic activity have drawn attention from researchers. Many strategies have been established and studied for the modification of TiO$_2$. Changing the electronic structure of TiO$_2$ by n-type doping increases the valence band energy level closer to the conduction band level. This band gap control enables the efficient utilization of solar energy [11,12]. Controlling TiO$_2$ facet alters the reactivity at the interface enhancing photocatalysis [13,14]. The construction of a
heterojunction with metals [15,16], or semiconductors [17–19], delays the recombination rate of electron-hole pairs as well as reducing the effective band gap [20]. Despite these efforts, the photocatalyst has a critical problem. It must need light as an essential driving force. An alternative modification is required to overcome this problem through the development of a photocatalyst that can work without illumination. Y. Takahashi and T. Tatsuma reported oxidative energy storage on a TiO$_2$ and Ni(OH)$_2$ bilayer film [21]. TiO$_2$ is an n-type semiconductor, while Ni(OH)$_2$ is a p-type. The combination of these two materials forms a p-n heterojunction. The layer of Ni(OH)$_2$ can store oxidative energy by changing its color from colorless to brown under UV illumination, whilst the stand-alone Ni(OH)$_2$ could not. Photo-oxidized Ni(OH)$_2$ can be reversibly changed to colorless Ni(OH)$_2$ by redox reaction or electrochemical process. Our previous work demonstrated the presence of oxidative energy storage in NiO incorporated with TiO$_2$ casting on TiO$_2$ as a bilayer film catalyst (NiO-TiO$_2$/TiO$_2$) by the electrochemical process [22]. The bilayer film catalyst was manufactured by a simple spin coating technique, which is excellent for controlling uniformity and thickness [23]. Not only was oxidative energy storage found but it also enhanced the photocatalytic activity in light compared to bare TiO$_2$ and NiO. Furthermore, the bilayer film catalyst showed catalytic activity without light after exposing the catalyst to light for one hour. This feature is similar to the concept of charging and discharging of batteries. The catalyst can work under illumination, while excessive photoenergy can be stored and re-emitted in dark conditions, so-called photo-chargeable. The previous bilayer film catalyst can be further optimized for photocatalytic activity and oxidative energy storage by adjustment of the synthesis condition. Therefore, in this report, we reviewed the photocatalytic activity in the presence of light and in the absence of light of NiO-TiO$_2$/TiO$_2$ bilayer film photocatalyst (BLF), which was prepared by a facile technique of layer-by-layer spin coating. The effect of NiO calcination temperature and ratio between TiO$_2$ and NiO on the degradation performance was investigated. Acid orange 7 (AO7) was selected as the organic molecule since it is commonly found in wastewater. It is an anionic azo dye with high color intensity even at low concentrations, which could inhibit the photosynthesis of marine plants. The degradation of this photo-chargeable catalyst can lead to sustainable wastewater treatment by the continuous use of renewable energy throughout the day and night.

2. Materials and Methods

2.1. Synthesis of NiO-TiO$_2$/TiO$_2$ Bilayer Film

A substrate used before the coating procedure was prepared by submerging a glass slide in cleaning solution (MICRO-90, Cole-Parmer Instrument Company, LLC, Vernon Hills, IL, USA) and was ultrasonicated. A solution containing 3 g of bis(2,4-pentanedionato)titanium (IV) oxide (reagent grade, TCI Co., Ltd., Tokyo, Japan) dissolved in 3 mL of ethanol (99.8%, Bangkok Liquor Co., Ltd., Bangkok, Thailand) was applied to the glass substrate by spin coating at 1500 rpm for 20 s. Then it was placed in an oven at a temperature of 400 °C for 1 h for calcination, resulting in a TiO$_2$ film. The weight of the TiO$_2$ layer was found to be 0.004 ± 0.001 g. After that, the precursors needed for the second layer coating were prepared. TiO$_2$ sol was made by diluting 1.4 mL of concentrated HNO$_3$ (70%, Merck KGaA, Darmstadt, Germany, Sigma-Aldrich Inc., Darmstadt, Germany) in 200 mL of deionized water. Then 16.7 mL of titanium isopropoxide (TIPP, 97%, Sigma-Aldrich, Inc., Darmstadt, Germany), as a precursor, was mixed with the prior solution under vigorous stirring for a couple of days until the solution became a clear solution. The resulting solution was dialyzed through a membrane to obtain TiO$_2$ sol at a pH condition of 3.5 ± 0.1. Nickel (II) hydroxide (99%, Sigma-Aldrich, Inc., Germany) was introduced to a calcination furnace for 1 h to form NiO particles. NiO obtained at different calcination temperatures were denoted as yNiO, where y is calcination temperature which is at 250 °C, 300 °C, 350 °C, and 400 °C. The solution for second layer coating was prepared by mixing 4 mL of the prepared TiO$_2$ sol, 0.16 mmol polyethylene glycol (100%, MW = 1000 g/mol, Wako Pure Chemical Industries, Ltd., Osaka, Japan) and different amounts of NiO of 4.7, 8.0, 12.0, and 15.7 mmol
to achieve NiO loading percentage by mole of 39%, 52%, 62%, and 68%, respectively. Then the solution was dropped onto the prepared TiO\textsubscript{2} film followed by spin-coating at the same condition as in the prior coating. Finally, it was calcined at the temperature at which NiO was obtained for 1 h to obtain a bilayer film catalyst (BLF). It was denoted as x-yBLF, where x is the loading percentage of NiO and y is the calcination temperature to obtain NiO particles. For instance, 52-300BLF has 52% NiO loading obtained by calcination at 300 °C. The second layer of the bilayer film weighed approximately 0.012 ± 0.003 g per glass slide. The pictorial outline of BLF preparation procedure is presented in Figure 1.

![Figure 1. Schematic of BLF preparation.](image)

### 2.2. Physical Characterization

The morphology of BLF was characterized by using a scanning electron microscope (SEM, S-4800, Hitachi Co., Tokyo, Japan) with an accelerating voltage of 2.0 kV. The crystallinity of synthesized films was confirmed by using an X-ray diffractometer (XRD, SmartLab, Rigaku Co., Ltd., Tokyo, Japan) with monochromatic Cu K\textalpha\ radiations (\(\lambda = 0.154\ nm\)) at 40 kV and 30 mA with angles ranging from 20° to 80°. The average particle size of NiO particles at different calcination temperatures was determined by a particle size analyzer (PSA, Mastersizer X, Malvern Panalytical Ltd., Malvern, UK). The zeta potential analyzer (Zetasizer model ZS, Malvern Panalytical Ltd., Malvern, UK) was used to find the point of zero charge (PZC) of bilayer films as well as the charge on the surface of catalysts across pH values.

### 2.3. Photocatalysis Experiments

The photocatalytic activity of BLF was investigated by the degradation of acid orange 7 (AO7, Tropaeolin No. 2, analytical grade, Fluka Chemical Corp., Gillingham, UK). A total of 200 mL of 20 ppm AO7 aqueous solution was added in a 500 mL beaker. The pH of the solution was adjusted to 3 using 0.5 M HCl. The photocatalyst glass slide was immersed in the solution for 15 h prior to light exposure to ensure that the adsorption of AO7 on the film reached saturation. Afterward, 5 UV-A lamps (200W Hg-Xe Lamp, LA-410 UV, Hayashi Tokei, Tokyo, Japan) equipped with a 365-nm bandpass at a light intensity of 5 mW/cm\textsuperscript{2} were turned on to start the photocatalysis. The solution was exposed to light for 2 h before the light source was turned off for another 2 h, achieving the first cycle of illumination. The second cycle of illumination subsequently followed the first cycle, achieving an 8 h experimental run. The photocatalysis cycles were carried out in a black box to prevent disturbances from other light sources. The operating condition of photocatalysis was kept at a stirring rate of 150 rpm and an operating temperature of 30 °C, which was controlled by a water bath equipped with a thermostat. The solution was sampled every hour during photocatalysis cycles for quantitative measurement using a UV-vis spectrophotometer.
The percentage of degradation of AO7 was calculated using Equation (1),

$$\text{% Degradation} = \left| \frac{C_n - C_{n-2}}{C_{n-2}} \right| \times 100$$  \hspace{1cm} (1)

where $C_n$ and $C_{n-2}$ are the concentrations at the time $n$ and $n - 2$, when $n = 2$ and 4 h. $C_0$ is the initial concentration at time $= 0$. Each experiment was triplicated to prevent anomalies. The mean and standard deviation were used for the data representation. The pictorial outline is presented in Figure 2.

Figure 2. Schematic of the photocatalytic degradation measurement setup.

3. Results and Discussion

3.1. Characterizations

The digital images showing the surface morphologies of the synthesized TiO$_2$ on a glass slide and 52-300BLF with different magnifications are shown in Figure 3. The TiO$_2$ layer was successfully uniformly coated on a glass slide confirmed by the good distribution of TiO$_2$ shown in Figure 3a,b. After the second coating, Figure 3c shows the clusters of NiO particles distributed over the first TiO$_2$ layer. It was confirmed that the second layer was coated on the first layer to form 52-300BLF. Figure 3d demonstrates that the 52-300BLF is a porous structure at higher magnification. These pores were formed by the removal of PEG during calcination. The pores seem to have two types of small pores and interparticle voids. These pores are crucial for dye adsorption, increasing the surface area and are the pathways for light to pass through to the first layer for photocatalytic activity.

The crystallinity of the samples was investigated by the XRD technique. The XRD patterns of 52-300BLF at different NiO loadings are presented in Figure 4a. It shows that TiO$_2$ and NiO peaks are in all 300BLFs with different NiO loadings. TiO$_2$ shows the anatase phase that can be described by the presence of main peaks at 2θ of 25.4°, 38°, 48°, 53.7°, and 55° where they are attributed to (101), (004), (200), (105), and (211) planes (JCPDS card no. 21-1272), while the NiO face-centered-cubic (FCC) structure is demonstrated at 2θ of 37.2°, 43.2°, 63.0°, and 75.2° corresponding to the (111), (200), (220), and (311), respectively (JCPDS card no. 075-0269). The structural properties of BLFs are summarized in Table S1. The difference between these spectra is that the sharpness and peak intensities of the NiO phase increase with the NiO content, while there is no phase change observed from the spectra. Furthermore, the average size of TiO$_2$ crystals increases as the amount of NiO loading increases. This could be due to the larger amount of NiO acting as a spacer between the TiO$_2$ crystals, which prevents them from contacting closely with each other. Figure 4b reveals the XRD spectra of 52% loading BLFs at different calcination temperatures of NiO. The peaks of NiO phase become sharper as the calcination temperature increases. This provides evidence that the size of NiO becomes larger at higher calcination temperatures. This is in accordance with the increase in the average crystallite size of NiO in the BLFs with the increase in the calcination temperature, Table S1. In addition, the results are in good agreement with the average particle size of NiO calcined at various temperatures,
shown in Figure 5a, which is determined by the particle size analyzer. The positive change in the particle size is ascribed to the agglomeration of NiO particles to form larger clusters at higher temperatures.

Figure 3. SEM micrographs of synthesized TiO$_2$ (a,b), and 52-300BLF (c,d) at the magnifications of 400× (left) and 20,000× (right).

Figure 4. XRD patterns of BLFs at: (a) different NiO loadings calcined at 300 °C and (b) different NiO calcination temperatures at 52% loading.

The surface charge of 52-300BLF under different pH conditions was measured using Zeta potential technique as presented in Figure 5b. The pH at the point of zero charge (pH$_{PZC}$) is 4.6. The pH below the pH$_{PZC}$ reveals the positively charged surface of BLF, while the pH above the pH$_{PZC}$ shows a negative surface. The positively charged surface is beneficial for AO7 adsorption, since it is an anionic dye where the negatively charged site is at the sulfonate group with a very low pK$_a$ [24]. The large difference between the positively charged surface on the adsorbent and the negatively charged adsorbate leads to adsorption through chemisorption. Thus, all photocatalytic degradation experiments were carried out at a pH of 3.
3.2. Photocatalytic Degradation

The photocatalytic activity of TiO$_2$ film and BLFs was tested by degradation of AO7 in 200 mL of 20 ppm AO7 at pH 3. The test was conducted in two subsequent cycles each of which had 2 h long UV-A illumination followed by another 2 h in the absence of light giving a total of 8 h. Figure 6a shows the results on the degradation of the TiO$_2$ film on a glass substrate and 52-300BLF describing that the degradation performance of BLF is superior to that of the TiO$_2$ film. The total degradation of the bilayer film in 8 h is approximately 50%, which is five-fold greater than that of the TiO$_2$ film. One of the possible reasons is that the TiO$_2$ film has a smoother surface than the bilayer film, as seen in the SEM micrographs (Figure 3). A rougher surface results in better adsorption, as there is a larger surface area. In addition, a rougher surface could enhance photocatalytic activity by increasing light absorptivity because of more contact points with incident light [25,26]. Another reason is that TiO$_2$ is an n-type semiconductor that has photocatalytic activity but is limited by electron-hole recombination, while NiO, a p-type semiconductor, is coupled with TiO$_2$ creating a type-II p-n heterojunction [27] in the BLF catalyst. Type-II photocatalytic activity is enhanced because of electron-hole pairs separation. By this means, the BLF catalyst can perform better than the standalone TiO$_2$. This is also in good agreement with previous reports [28,29]. Furthermore, Figure 6b reveals that BLF still has the ability to further degrade AO7 even in the absence of light (at 4 and 8 h), whereas that is not the case with only TiO$_2$. This gives insight into the characteristics of the NiO-TiO$_2$/TiO$_2$ BLF catalyst during light exposure. That is, not all light energy is used for degradation, but some parts are stored within the catalyst. Without exposure to light, the degradation still undergoes feasibly without external work. These behaviors, depending on the illumination, are similar to those of charging and discharging processes. This special feature belongs to BLF catalysts composing NiO-TiO$_2$ and TiO$_2$ layers, while it is not the case for the naked layers of TiO$_2$ and NiO-TiO$_2$. This energy storage and photo-chargeable characteristics were demonstrated in the previous report [22] by the electrochemical process and degradation under light and dark conditions, respectively. Therefore, further investigations focus on the optimal amount of NiO and the calcination temperature to obtain NiO particles to prepare the BLF catalyst for AO7 degradation with the highest energy storage.
3.3. Effect of NiO Loading

One of the crucial factors for the preparation of the BLF catalyst is the ratio of NiO to TiO$_2$. The effect of NiO loading in the second layer of the catalyst on the degradation performance was then investigated. The loading amount was varied at 39, 52, 62, and 68 mol% while the calcination temperature to obtain NiO particles was set at 300 °C. Afterward, their photocatalytic activity was tested. The results are presented graphically in Figure 7a. At the lowest NiO content at 39%, the total degradation is 18%. Increasing the NiO amount to 52% achieves the maximum total degradation of about 50%, further increasing NiO loading to 62% and 68% reduces total degradation to 40% and 30%, respectively. At 39% loading, there might be an insufficient amount of NiO to couple with TiO$_2$, thus the separation of the electron-hole pairs by p-n heterojunction could not be fully functioned, while at the higher loadings there might be an agglomeration of NiO particles making large clusters of them. Large particles may be beneficial for charge transport because of longer diffusion path, and less collision with boundaries, hence it reduces electron-hole pair recombination [30]. However, too much NiO loading could cause large particles, which can inhibit the light reaching the TiO$_2$ surface to activate the photocatalytic activity. In addition, the large particle size of NiO may reduce the surface area to contact with AO7 molecules, reducing the overall photocatalytic activity. To demonstrate the degradation performance in the dark, Figure 7b is plotted to compare the degradation in the presence of light and in the dark of each cycle. Among these catalysts, the catalyst with 52% NiO loading has the best overall degradation performance in both cycles. Under light, 52-300BLF achieves 22.0% and 18.4% degradation for the first and second cycles, respectively. Likewise in the dark, it still has the highest degradation which is 13.6 and 5.2 for the first and second cycles. All catalysts have a similar trend in which there is a decrease in the degradation in the second cycle compared to the first cycle. This decrease might be due to the lower concentration of AO7 in the initial state since the adsorption and the photocatalysis are concentration-dependent factors.

3.4. Effect of NiO Calcination Temperature

The amount of NiO in the BLF catalyst could alter the photocatalytic activity but also the characteristics of NiO particles. Here, the additional four catalysts were manufactured by fixing the NiO loading at 52% but varying the calcination temperature to obtain NiO particles. The same photocatalytic activity was carried out. The results are shown in Figure 8. Increasing the calcination temperature from 250 °C to 350 °C does not alter the degradation to any significant extent. At 2, 4, 6, and 8 h of degradation, three catalysts perform comparably. After 8 h of degradation, AO7 is degraded to 50.7%, 52.2%, and 52.5% in the solution with 52-250BLF, 52-300BLF, and 52-350BLF, respectively. While 52-400BLF shows the worst performance at 12% degradation after 8 h. This could be explained by...
the fact that at the higher calcination temperature, NiO particle size becomes larger, as confirmed by the XRD results in Figure 4b and the particle size analysis in Figure 5a. At the same NiO loading on the film, NiO with a larger size might have fewer separated clusters than those of smaller NiO. It reduces both surface area and the number of photocatalytic sites for AO7 degradation. Thus, the overall photocatalytic effect is reduced. Not only the overall performance but also its activity in the dark follows the same trend. Figure 8b demonstrates the percentage degradation in light and dark conditions for each cycle. Although 52-250BLF, 52-300BLF, and 52-350BLF show comparable degradation under both conditions, 52-300BLF has the highest degradation in the dark in both first and second cycles. Hereby, the calcination temperature of 300 °C is optimal to obtain NiO for the preparation of BLF catalyst.

![Figure 7](image1.png)

**Figure 7.** Photocatalytic degradation of four different NiO loading BLF catalysts by: (a) relative concentration over time and (b) degradation in light and dark conditions for each cycle.

![Figure 8](image2.png)

**Figure 8.** Photocatalytic degradation of BLF catalysts at four different calcination temperatures to obtain NiO by: (a) relative concentration over time and (b) degradation in light and dark conditions for each cycle.

### 3.5. Proposed Mechanism for AO7 Degradation

From the previous sections, 52-300BLF was chosen as the best catalyst for AO7 degradation. It not only has excellent performance under light exposure, but it also outperforms in the absence of light. The photocatalytic activity of 52-300BLF, which is superior to that of the TiO$_2$ film, could be explained by the presence of p-n heterojunction of semiconductors. The detailed mechanism inside this p-n heterojunction could be elucidated by the following: under illumination, the light energy that is equal to or greater than the band gap of NiO and TiO$_2$ generates electron-hole pairs. Light absorption by the p-n heterojunction affects the drifting of the minority on each side of n-type TiO$_2$ and p-type NiO. Minority holes from
the n-type TiO$_2$ are then transferred to p-type NiO while the minority electrons from p-type NiO drift to the n-type TiO$_2$, as shown by Equation (2). This enhances the electron-hole pair separation as well as minimizes the recombination. Photogenerated electrons on the TiO$_2$ cause the reduction on the dissolved O$_2$ to form superoxide ions that further react with proton and water molecules to form hydroxyl radicals as active species for AO7 degradation (Equations (3)–(5)). At the same time, photogenerated holes at the p-type NiO give rise to the oxidation of water molecules to form hydroxyl radicals. Then, they react with the adsorbed AO7 molecules on the surface, resulting in the dye degradation as shown in Equations (6) and (7). Moreover, AO7 might be reduced or oxidized directly to electrons and holes to form reduced and oxidized products, respectively, Equations (8) and (9). However, not all photogenerated holes are used for degradation; some are kept as the reactive holes, which are then stabilized by the intercalation of anions, such as OH$^-$ and Cl$^-$, provided by the electrolyte. This process is similar to a charging process in a battery. These reactive holes correspond to the degradation in the absence of light. An illustrated summary of photocatalysis under UV illumination is shown in Figure 9a. During the charging process, there is an increase in the electric field as the hole concentration increases at the p-type NiO. After turning off the light source, the drifting of minorities is no longer enhanced, but the diffusion of majorities becomes dominant. The holes in the p-type NiO diffuse to the n-type TiO$_2$ whilst the electrons from the n-type TiO$_2$ diffuse to another side, presented in Figure 9b. This decreases the electric field of the p-n heterojunction back to their equilibrium feasibly as it discharges. This makes the NiO side less positive so that stabilized holes by the anionic intercalation are released as the mobile holes (Figure 9c). The mobile holes cause the degradation of dye molecules in the dark following the Equations (6)–(8). The presence of oxidative energy storage in NiO coupled with TiO$_2$ on the TiO$_2$ film was also proven by electrochemical measurements in our previous report [22].

\[
\text{NiO} - \text{TiO}_2 + \text{hv} \rightarrow e^- (\text{TiO}_2) + h^+ (\text{NiO}) \quad (2)
\]
\[
\text{O}_2 + e^- (\text{TiO}_2) \rightarrow \cdot \text{O}_2^- \quad (3)
\]
\[
\cdot \text{O}_2^- + \text{H}^+ \rightarrow \cdot \text{HO}_2 \quad (4)
\]
\[
\cdot \text{HO}_2 + \text{H}_2\text{O} \rightarrow \cdot \text{OH} + \text{H}_2\text{O}_2 \quad (5)
\]
\[
\text{H}_2\text{O}_{\text{ads}} + h^+ (\text{NiO}) \rightarrow \text{H}^+ + \cdot \text{OH} \quad (6)
\]
\[
\text{Dye} + \cdot \text{OH} \rightarrow \text{degradation products} \quad (7)
\]
\[
\text{Dye} + h^+ (\text{NiO}) \rightarrow \text{oxidized products} \quad (8)
\]
\[
\text{Dye} + e^- (\text{TiO}_2) \rightarrow \text{reduced products} \quad (9)
\]
Figure 9. Schematic of: (a) photocatalysis on type-II heterojunction photocatalysts, (b) charging, and (c) discharging processes for AO7 degradation in light and dark conditions.

4. Conclusions

The effect of NiO preparation conditions coupling on TiO$_2$ film on the AO7 degradation was revealed in this report. The NiO-TiO$_2$/TiO$_2$ BLF catalysts show a superior performance to the ordinary TiO$_2$, not only in the presence of light, but also in the absence of light. This is due to the enhancement of photocatalytic activity by the p-n heterojunction between the p-type NiO and the n-type TiO$_2$. The photocatalytic activity in the dark was possible because of the intercalation of anion to stabilize the photogenerated holes during the illumination, which were then released in the absence of light. The overall degradation was about five folds greater than the bare TiO$_2$ film. The optimal condition was investigated to obtain the best-performing BLF in AO7 degradation. The BLF with 52% NiO loading with a calcination temperature of 300 °C showed outstanding overall degradation than other BLFs in the light and in the dark conditions. The results gave insights into the dark photocatalysis and the optimal conditions to prepare BLF catalysts. Furthermore, an advanced photocatalyst that maintains a high working efficiency under unfavorable conditions could be developed through further condition adjustment such as the pH of the electrolyte and the type of counterions.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings13010141/s1. Table S1: Average crystallite size, microstrain, dislocation density, lattice constants, and volume cell of BLF photocatalysts. References [31–33] are cited in the Supplementary Materials.

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