Research Article

Synthesis of Highly Active Heterostructured Al$_2$TiO$_5$/TiO$_2$ Photocatalyst in a Neutral Medium

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In this work, heterostructured catalyst Al$_2$TiO$_5$/TiO$_2$ (ATO/Ti) was synthesized by a two-step method: low-temperature sol-gel process along with hydrothermal treatment in a neutral medium. Characteristics of the fabricated catalyst were analyzed by various techniques including X-ray diffraction, Fourier transform infrared spectroscopy, Brunauer-Emmett-Teller adsorption, UV-Vis diffuse reflectance spectroscopy, energy-dispersive X-ray spectroscopy, field emission scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, and the point of zero charges. The content of ATO strongly affected the activity of ATO/Ti catalysts for photocatalytic degradation of cinnamic acid (CA). The catalyst, in which 33% TiO$_2$ was replaced by ATO (33ATO/Ti), exhibited the highest activity for the removal of CA. Compared with the bare titanium oxide synthesized in water (TiO$_2$(w)) as well as Al$_2$TiO$_5$ (ATO), the hybrid 33ATO/Ti catalyst exhibited the enhanced photocatalytic activity in the CA degradation under ultraviolet light. The enhancement in the catalytic activity of ATO/Ti could be related to the increase of the specific surface area and the reduction of bandgap energy obtained from the hybridization of TiO$_2$(w) and ATO. The factors as the catalyst dosage ($C_{\text{cat}}$), the airflow rate ($Q_{\text{air}}$), and the solution initial pH (pH) affected the CA removal efficiency were studied on 33ATO/Ti catalyst. The optimum condition for photodegradation efficiency of CA was found to be at $C_{\text{cat}} = 0.75$ g L$^{-1}$, $Q_{\text{air}} = 0.3$ L min$^{-1}$, and pH = 3.8. The highest 60-minute removal efficiency of CA reached 77.1% on 33ATO/Ti compared with 67.1% and 30.4% on TiO$_2$(w) and on ATO, respectively. The recyclability of the 33ATO/Ti was also measured at the optimal parameters. The results showed that, compared with TiO$_2$, the hybrid catalyst was easier to recover and reuse, and its activity decreased by 35% after 6 continuous cycles.

1. Introduction

Phenolic compounds are a member of the largest groups of environmental pollutants as gallic acid, protocatechuic acid, vanillic acid, syringic acid, and cinnamic acid. They were widely used in the agroindustrial wastewaters from cork, olive oil mills, and wine distilleries as well as antimicrobial agents [1, 2]. However, the presence of the remaining phenolic in the water has been considered as priority pollutants due to their high toxicity for human health and nonbiodegradability on the environment at the extremely low concentration [3]. Therefore, the elimination of phenolic compounds from wastewater is the current attention. CA was known as a model of the persistent phenolic acids in polluted water.

Titanium oxide has been considered as a conventional photocatalyst and attracted attention in photocatalytic applications thanks to its low cost, high stability, and environment-friendly semiconductor [4]. However, the limitations of titanium oxide are UV light-activated and high electron-hole recombination [5]. Perovskites were evaluated as potential semiconductors in photocatalytic reactions under UV and visible lights based on low bandgap energy and good
chemical stability [6]. Nowadays, perovskite photocatalysts have been studied extensively because of their promise for being visible light active [7]. Among these, titanate perovskites have been studied for photocatalytic applications for a long time. Most of the titanate perovskites are characterized by relatively low bandgap energies (approximately 3.0 eV) and exhibit excellent photocatalysts under UV light [8]. The perovskite titanate also provides good photo-stability and corrosion resistance in aqueous solutions, making them suitable photocatalysts for the degradation of pollutants in water [7]. Additionally, perovskite titanate was considered a promising photocatalyst for water splitting, dye degradation, and CO₂ or NOₓ reduction [9].

Heterostructure materials have been developed to accelerate the separation of photogenerated electrons and holes [10]. The heterogeneous catalysts exhibited advantages like high performance, easy recovery, and cost-effectiveness [11]. One of the recent heterogeneous photocatalysts was materials from the hybridization of titanium oxide with perovskites to enhance the photocatalytic properties [12, 13]. Wu et al. demonstrated that the photoelectrochemical performance of the TiO₂/SrTiO₃ catalyst was enhanced thanks to the charge separation and hole transportation [12]. A similar trend has been mentioned in the study of water splitting. The results elucidated that SrTiO₃-TiO₂ boosted the separation efficiency of the photogenerated charge carriers [14]. Also, the porous NiTiO₃/TiO₂ catalyst, synthesized by a hydrothermal route, exhibited excellent performance such as high surface area, high light absorption, and efficient charge separation for photocatalytic hydrogen generation [13]. Huang et al. found that NiTiO₃ was an effective cocatalyst, which improved the photocatalytic activity of TiO₂ on the heterostructural NiTiO₃/TiO₂ nanotubes [15].

In our previous research [16], the synthesis of titanium oxides by the hydrothermal method from titanium isopropoxide (TTIP) in different media including acid, neutral, and alkali was carried out. The results showed that physicochemical characteristics and the photocatalytic activity of the obtained TiO₂ depend on the synthetic environment. A remarkable result indicated that the point of zero charge (PZC) value of the produced TiO₂ was determined by the synthetic environment. The higher pH of the synthetic medium was, the greater the PZC value of the sample achieved. Also, there was a difference in phase composition, physicochemical properties, and photocatalytic activity for the prepared TiO₂ in different media.

The aluminum titanate AlₓTiO₅ (ATO) material with pseudobrookite structure has attracted considerable attention in water purification due to the removal of turbidity and pathogenic microorganisms [17, 18]. To date, AlₓTiO₅ has been recognized as an innovative material for photodegradation in wastewater treatment. However, in most studies [19–21], AlₓTiO₅ was synthesized by the sol-gel method at high temperature (>900°C). In our previous investigation [22], a nanostructured ATO-rich catalyst was synthesized by the sol-gel method from aluminum nitrate, titanium isopropoxide, and citric acid at relatively low temperatures (700°C). The obtained ATO showed bandgap energy of 3.18 eV, which was significantly lower than that was reported in [23] and higher than that was found by Bakhshandeh et al. [21]. Therefore, the synthesis ATO was preferably used as UV-photocatalyst. However, its activity was much lower than that of the TiO₂ and commercial P25 TiO₂ [22]. The combination of ATO and TiO₂ has been expected to form a hybrid photocatalyst with high photocatalytic activity and easy to reuse.

In this work, heterostructured ATO/Ti catalysts were synthesized by the sol-gel method in the neutral medium combined with the hydrothermal treatment. The use of water as the neutral medium in the synthesis of ATO/Ti hybrid materials has an environmental benefit. The physicochemical characteristics and the photocatalytic activity of the obtained ATO/Ti heterostructures in the photodegradation of CA solution under ambient conditions were investigated. Additionally, there was a detailed comparison in the characterization as well as the photocatalytic performance of the ATO/Ti catalyst hydrolyzed in the neutral medium and the acid medium.

2. Materials and Methods

2.1. Catalyst Preparation. Aluminum titanate AlₓTiO₅ (ATO) was synthesized by the low-temperature sol-gel technique according to the optimal process identified in the study [22]. Heterostructured ATO/Ti catalysts were prepared by the hydrothermal method in the water. Titanium (IV) iso-propoxide (Ti(OH)₃(CH₃)₂, Merck, 97.0%) was used as a precursor and dropwise to water with the ratio volume of 3/40 v/v. The obtained mixture was continuously stirred for 1 h to produce a homogeneous solution. In the next stage, x = 0.27, 0.40, 0.80, and 1.60 g of ATO was added to the resulting solution and followed by hydrolysis in the autoclave at 160°C for 12 h. The resulting precipitate was washed with distilled water and ethanol three times and dried at 60°C for 12 h. The catalysts were denoted as yATO/Ti, representing the ATO content of y = 25, 33, 50, and 67 wt.% in the hybrid catalysts.

2.2. Catalyst Characterization. X-ray diffraction (XRD) measurements were performed on Bruker D2 Phaser X-Ray Diffractometer with Cu Kα radiation and recorded in 2θ = 10 – 80°. The Raman spectra were obtained at room temperature with a laser Raman spectrometer (Invia, Renishaw, UK). Nitrogen adsorption-desorption isotherms were determined by using a Nova 2200e instrument. The specific surface area of samples was calculated according to the Brunauer-Emmett-Teller (BET) nitrogen adsorption isotherms. The elemental analysis of the synthesized nanoparticles was performed using the EDX spectrum on the JEOI JST-IT 200 instrument. Hitachi S4800 field emission scanning electron microscopy (FESEM) and a JEOL JEM 1400 transmission electron microscopy (TEM) apparatus were used to investigate the morphology and surface properties of obtained materials. The characterization of functional groups of materials was measured using Fourier transform infrared (FTIR) in the range from 400 to 4000 cm⁻¹. The point of zero charge (PZC) of the samples was determined by the salt addition method [24]. The bandgap energy of
the photocatalysts was determined by UV-Vis diffuse reflectance spectroscopy (DRS) on a Varian Cary 5000 UV-Vis-NIR spectrophotometer with an integrating sphere in the range of 200-800 nm.

2.3. Catalytic Activity. The photocatalytic activity of samples was studied by the batch method as described in [22]. Briefly, the reaction solution volume 250 mL of cinnamic acid concentration 50 mg L\(^{-1}\) was stirred in the dark for 40 min to establish the adsorption/desorption equilibrium before exposure to the UV light irradiation of 36 UV-A Engin L21-00 U600 lamps (\(\lambda \approx 350 – 400\) nm, concentrated at 365 nm) to carry out the reaction. The reaction solution was separated by filtration and analyzed using a UV-visible spectrophotometer on UV-1800 (Shimadzu) at 272 nm. The influence of the operation parameters including the catalyst dosage \((C_{\text{cat}} = 0.5, 0.75, 1.0, \text{and } 1.25 \text{ g L}^{-1})\), the initial pH solution \((\text{pH} = 3.0, 3.8, 5.0, 7.0, \text{and } 9.0)\), and the supply air flow rate \((Q_{\text{air}} = 0.1, 0.3, \text{and } 0.5 \text{ L min}^{-1})\) was surveyed. The recyclability of catalysts was tested at the optimized conditions until the reaction solution volume 250 mL of cinnamic acid concentration 50 mg L\(^{-1}\) was removed at the end of each batch and replaced by a fresh CA solution to conduct the photocatalytic reactions in succession.

3. Results and Discussion

3.1. Physicochemical Characteristics of Catalysts. On the XRD pattern (Figure 1(a)), TiO\(_2\) in the anatase phase appeared at the 2\(\theta\) = 25.2°, 38.2°, 48.3°, 54.3°, 63.1°, and 75.5° (JCPDS 21-1272) with the strongest intensity at 2\(\theta\) = 25.2°. Other phases of TiO\(_2\) such as rutile or brookite were not observed on the samples. Furthermore, diffraction peaks at 20 values of 18.9°, 26.6°, 33.7°, 42.0°, 42.6°, and 50.7° corresponding to the phase of ATO (JCPDS 26-0040) were also observed. As the ATO content increased, the intensity of the characteristic peak of ATO was stronger. Compared with samples prepared in the acid medium (denoted as ATO/Ti(a)) [25], the phase composition of TiO\(_2\) in obtained ATO/Ti significantly changed. TiO\(_2\) only existed in the anatase phase on ATO/Ti catalysts, whereas there was an existence of anatase (A) and rutile (R) phases on ATO/Ti(a) samples. Furthermore, the ratio of A:R increased from 70:30 to 100:0 when the ATO content in the composite increased from 25% to 75% that was found. The synthesized 67ATO/Ti(a) catalyst, whose anatase: rutile ratio of 88:12, exhibited the best activity. Similarly, the pure TiO\(_2\)(w) sample only contained the anatase phase, while the TiO\(_2\)(a) sample obtained in an acidic medium consisted of 65% A and 35% R phase [16]. In comparison with the XRD pattern of bare ATO [22], the intensity of the characteristic peaks of ATO became weaker after hybridization with TiO\(_2\)(w), which may due to the poorer crystallinity [26]. The reduced crystallinity of the anatase phase in ATO/Ti catalysts was accompanied by the increased defects. This result was beneficial to hinder the recombination of photogenerated charges [27]. Thus, the photocatalytic activity of the hybrid catalyst was considerably enhanced.

The crystal size of the anatase and ATO phase was calculated by the Scherrer equation at 2\(\theta\) = 25.2° and 2\(\theta\) = 26.6°, respectively (Table 1) [28]. The result indicated that the crystal size of the anatase phase in heterostructure materials was approximately 35.0 nm, nearly the value in bare TiO\(_2\) (34.8 nm). The crystal size of the anatase phase in this study was twice that of the sample prepared in an acid medium, being from 17 to 19 nm [25]. The obtained results showed that the synthetic medium had an obvious impact on the composition and properties of TiO\(_2\) in ATO/Ti hybrid materials. Meanwhile, the average crystal size of the ATO phase in the three samples ATO, ATO/Ti, and ATO/Ti(a) was approximate, varying in the narrow range 33–34 nm. The reason is that ATO in all three cases was presynthesized by the same process, describing in [22].

Raman spectra of ATO/Ti catalysts were illustrated in Figure 1(b). The main Raman bands for the TiO\(_2\) phase identified at 147, 208, 402, 517, and 639 cm\(^{-1}\). The symmetric stretching vibration of O-Ti-O was characterized by the \(E_g\) peak. Meanwhile, the \(B_{1g}\) peak assigned to the symmetric bending vibration of O-Ti-O, and the \(A_{1g}\) peak was the antisymmetric bending vibration of O-Ti-O. In comparison with the typical Raman bands of the anatase phase: 138 cm\(^{-1}\) \((E_g)\), 191 cm\(^{-1}\) \((E_g)\), 391 cm\(^{-1}\) \((B_{1g})\), 510 cm\(^{-1}\) \((A_{1g})\), and 634 cm\(^{-1}\) \((E_g)\) [29], the shifts were observed on Raman spectra. The shifts of Raman bands and the poorer crystallinity in ATO/Ti catalysts indicated that the heterostructured composite was formed.

The presence of hydroxyl groups and adsorbed water on the surface of ATO/Ti catalysts were analyzed by the FTIR method. According to Wang et al., the formation of hydroxyl radicals, the minimization of electron-hole recombination, and the enhancement of photocatalytic activity were directly related to hydroxyl groups and adsorbed water [30]. As shown in Figure 2, a wide peak at 2900-3700 cm\(^{-1}\) originated from stretching vibrations of OH groups. Furthermore, the bending vibration of O-H-O appeared at 1626 cm\(^{-1}\) [31]. The attribution of Ti-O and Al-O fluctuated in the range of 400-800 cm\(^{-1}\) [32]. The intensity of the peak characteristic for OH groups and adsorbed water decreased with increasing in the ATO content. As the result, the high ATO content on ATO/Ti could be unfavorable for the photocatalytic reaction [30]. The vibration of OH groups and the adsorbed water on ATO/Ti catalysts was stronger than that of ATO/Ti(a) [25]. Therefore, ATO/Ti catalysts could be more favorable for the photocatalytic reaction.

Figure 3 describes FESEM images of the obtained materials. FEEM image shows that ATO exists in the form of large blocks ranging in size between 50 and 500 nm (Figure 3(a)). The TiO\(_2\)(w) sample only contains the anatase phase, while the TiO\(_2\)(a) sample obtained in an acidic medium consisted of 65% A and 35% R phase [16]. In comparison with the XRD pattern of bare ATO [22], the intensity of the characteristic peaks of ATO became weaker after hybridization with TiO\(_2\)(w), which may due to the poorer crystallinity [26]. The reduced crystallinity of the anatase phase in ATO/Ti catalysts was accompanied by the increased defects. This result was beneficial to hinder the recombination of photogenerated charged [27]. Thus, the photocatalytic activity of the hybrid catalyst was considerably enhanced.
diameter. The square-shaped particles are arranged to form empty cages. Meanwhile, the spherical particles are aggregated in pistil shape blocks with a diameter of 50-150 nm and disperse inside the empty cages. As the ATO content increases, the density of the spherical particle rises. It can be assumed that square-shape particles are TiO2, and quasisphere-like particles are ATO.

HRTEM has been employed to characterize the shape, size, and morphology of the 33ATO/Ti sample. Atomic planes and lattice fringes were visible, confirming the crystalline nature of the 33ATO/Ti catalyst (seen in Figure 4). It can be observed the dark-color, quasisphere-like particles about 3-5 nm in size are attributed to ATO particles and bright thin slits, 1-2 nm thickness, characterized by TiO2. The inset in Figure 4 showed that the (101) plane of the anatase TiO2 established the majority in the structure of TiO2 with the d-spacing of 0.35 nm. From the SEM and HRTEM images, it can be seen that TiO2 plates in hybrid materials have dispersed ATO into small particles, as the ATO particle size reduced from 10-20 nm to about 5 nm. As a result, the specific surface area of the hybrid material is significantly higher than that of ATO and TiO2(w), as shown in Table 1. At the same time, the specific surface area of ATO/Ti synthesized in water was also higher than that of samples prepared in the acid environment (56-93 m2g–1) [25]. This may be related to the difference in morphology of the two hybrid materials. The ATO/Ti(a) sample existed in quasisphere-like nanoparticle size ranged from 30 to 70 nm [25], while ATO/Ti(w) existed in form of 5 nm spherical particles dispersed inside the square-shaped cages.

However, the specific surface area (S\textsubscript{BET}) of the ATO/Ti hybrid material depends on its composition. The specific surface area increased from 18.1 m2g–1 to 135.1 m2g–1 when the ATO content increased from 0% to 25% and reached the maximum value of 209.3 m2g–1 at the ATO content of 33%. However, further increase in the ATO content up to 50% of the specific surface area decreases. Also, the pore volume of 33ATO/Ti reached the highest value of ATO/Ti catalysts (Table 1). This can be explained by the optimal composition of two structural forms in the 33ATO/Ti sample, which facilitates the high dispersion of ATO particles into the TiO2.

Table 1: The crystalline size of the TiO2 anatase at 2θ = 25.2° (d\textsubscript{Ti}) and Al2TiO5 at 2θ = 26.6° (d\textsubscript{ATO}) from the XRD pattern; the specific surface area (S\textsubscript{BET}), the pore volume (V\textsubscript{pore}), and the pore size (d\textsubscript{pore}) from BET adsorption isotherm, the bandgap energy (E\textsubscript{g}), and absorption wavelength (λ) from UV-Vis diffuse reflectance spectra of the ATO/Ti catalysts.

| Catalyst | d\textsubscript{Ti} (nm) | d\textsubscript{ATO} (nm) | S\textsubscript{BET} (m2g–1) | V\textsubscript{pore} (mLg–1) | d\textsubscript{pore} (nm) | E\textsubscript{g} (eV) | λ (nm) |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| ATO [22] | —               | 33.6            | 18.1            | —               | 2.80            | 3.42            | 430             |
| TiO2(w) [16] | 34.8            | —               | 13.8            | —               | 2.00            | 3.14            | 395             |
| 25ATO/Ti | 34.8            | 33.5            | 135.1           | 0.081           | 1.78            | 3.07            | 404             |
| 33ATO/Ti | 35.0            | 33.4            | 209.3           | 0.268           | 2.40            | 3.06            | 405             |
| 50ATO/Ti | 34.8            | 33.4            | 103.5           | 0.064           | 1.84            | 3.04            | 408             |

Figure 1: XRD patterns (a) and Raman spectra (b) of obtained ATO/Ti catalysts.

Figure 2: FTIR spectra of ATO/Ti catalysts.
empty cage that leads to the highest pore volume and specific surface area. Increasing the ATO content in ATO/Ti samples from 33% to 50% led to an increase in the size and density of ATO spherical particles. At the same time, the density of the TiO₂ square-shaped particles reduced, and they are less orderly arranged, as seen in Figure 3. This may be related to, when the ATO content is too large (50%), the number of TiO₂ plates that are not enough to disperse it into small particles.

The elemental signals of the catalysts as TiO₂(w), ATO, and 33ATO/Ti were analyzed by EDX (Figure 5). Peaks at 2.2, 4.5, and 4.9 keV were assigned to the Ti element while two peaks at 2.6 and 1.5 keV were linked to the binding energies of O and Al, respectively. Additionally, the EDX
spectrum determined the presence of elements including Al, Ti, and O on the synthesized catalysts (Table 2). The obtained results confirmed the formation of heterostructured catalysts. As it follows from Table 2, the weight composition of the elements determined based on the EDX spectrum of the samples is quite consistent with the calculated data. Specifically, for the TiO$_2$ sample, the actual weight ratio of Ti : O is 59.4 : 40.6 compared to the calculated ratio 58 : 42. For the ATO sample, the actual weight component of Ti is 6.7% higher compared to the calculated result, while that for the Al, in contrast, is 9.7% lower. The most likely cause is the existence of small amounts of anatase TiO$_2$ in the ATO-rich material, as found in previous research [17]. For 33ATO/Ti hybrid materials, the actual weight component of Ti was approximately 10% higher than the calculated one, while that of Al was about 5 w% lower. This may be related to the encapsulating of ATO sphere-like particles by TiO$_2$ square-shaped plates as seen in the HR-TEM image, resulting in Ti element enrichment on the surface.

Figure 6 depicts N$_2$ adsorption-desorption isotherms of the as-prepared catalysts. The N$_2$ adsorption-desorption isotherms of the as-prepared 33ATO/Ti nanocomposites exhibited IV nitrogen isotherm with a hysteresis loop, indicating the mesoporous features [33]. Furthermore, it shows H2-type hysteresis loops distributed in the whole relative pressure region, which due to the irregular morphology and uneven pore size distribution caused by the heterostructure of obtained material [34]. The results of TEM and adsorption-desorption isotherms indicated that there was an integration of the anatase with the ATO to form heterostructured material.

The UV-vis diffuse reflectance spectra of the as-prepared catalysts were shown in Figure 7. It can be seen that the absorption of the ATO/Ti catalyst was located in the UVA light region with the absorption wavelength ranged from 404 to 408 nm (Table 1). The bandgap energy was found to be 3.07, 3.06, and 3.04 eV for 25ATO/Ti, 33ATO/Ti, and 50ATO/Ti, respectively, which is lower than that of ATO (3.18 eV), TiO$_2$ (3.14 eV), and approximate to ATO/Ti(a) [25]. These results showed that heterostructured materials have lower bandgap energy than the parent materials, but the $E_g$ value depends weakly on the composition of materials. According to Azarniya et al., the hybridization of Al$_2$TiO$_5$ with TiO$_2$ formed new bonds to vary the bandgap
values and increase the photodegradation efficiency of methylene blue [35].

The zeta potential of 33ATO/Ti versus the pH of the different solutions and the pH of the CA is indicated in Figure 8. The synthesized 33ATO/Ti catalyst had pH_{PZC} of 6.4, approximate to the PZC of ATO (6.2) [22], lower than that of TiO_2(w) (7.24) [16], and higher than that of ATO/Ti(a) (4.6) [25].

3.2. Activity of Catalysts. Figure 9 shows the CA removal efficiency for 60 min (X_{60}) on ATO/Ti catalysts with different amounts of ATO. The value of X_{60} increases from 66.9% to 77.1% when the ATO content increases from 25% to 33%. However, the X_{60} value gradually decreased to 66.1% and 55.1% as the ATO content continues to rise to 50% and 67%. The highest photocatalytic activity toward CA removal of the 33ATO/Ti sample may be due to its highest specific surface and pore volume, relatively high contents of hydroxyl groups on the surface, and the best distribution of ATO in the ordered TiO_2 cages as seen in the FESEM image (Figure 3). It was observed that the breakdown of the order structure of TiO_2 cages and the formation of the large ATO blocks can be correlated with an increase in the ATO content at 50% and 75%. Thus, the reduction in the photocatalytic activity was due to a decline in the specific surface area and the hydroxyl groups’ density on the surface.

| Catalyst      | Al  | Ti  | O   |
|---------------|-----|-----|-----|
| TiO_2(w)      | —   | 59.4| 40.6|
| ATO           | 19.2| 31.7| 49.1|
| 33ATO/Ti      | 19.1| 39.4| 41.5|

**Table 2: The element composition from the EDX spectrum.**

**Figure 5: EDS mapping and EDX spectrum of the catalysts: (a) TiO_2(w), (b) ATO, and (c) 33ATO/Ti.**
As shown in Figure 10(a), on the 33ATO/Ti, the photocatalytic activity for CA degradation of the 1.00 gL\(^{-1}\) dosage was higher than those obtained at other photocatalyst dosages. The results may be explained by the surface active sites of ATO/Ti and the phenomenon of light scattering. A lack of active sites for CA degradation at 0.50 gL\(^{-1}\) dosage caused the low conversion. On the other hand, a higher dosage (1.25 gL\(^{-1}\)) caused the aggregation of the photocatalyst and interception of the light, which was considered the main reasons to reduce the photocatalytic activity [36, 37]. Additionally, there

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**Figure 6:** Nitrogen adsorption-desorption isotherms on 33ATO/Ti catalyst (a) and the pore size distribution of the ATO/Ti catalysts (b).

**Figure 7:** UV-Vis diffuse reflectance spectra and Tauc plot of catalysts: TiO\(_2\)(w), ATO, 25ATO/Ti, 33ATO/Ti, and 50ATO/Ti.

**Figure 8:** The point zero charge of the 33ATO/Ti catalyst.

**Figure 9:** The CA removal efficiency for 60 min (\(X_{60}\)) in photocatalytic reaction on ATO/Ti catalysts at pH = 3.8, \(C_{cat} = 0.75\) gL\(^{-1}\), \(Q_{air} = 0.3\) Lmin\(^{-1}\), and \(T = 25^\circ\)C.
was an insignificant change when the photocatalyst dosage increased from 0.75 to 1.00 gL\(^{-1}\). Thus, the 33ATO/Ti dosage of 0.75 gL\(^{-1}\) was chosen as the optimal dosage.

Figure 10(b) indicates that the CA photodegradation efficiency strongly depended on the solution’s initial pH. The dependence of the CA degradation efficiency on the solution’s initial pH is extreme. The 60-minute removal efficiency reached a maximum of 77.1% at pH 3.8. The isoelectric point of 33ATO/Ti was determined to be 6.4 (Figure 7). At pH values less than pH = 6.4, the surface 33ATO/Ti was positively charged, whereas higher pH values promoted the formation of negative charge on the 33ATO/Ti. At the pH lower than its pKa value (4.44) [38], CA was deprotonated to form anion \(\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{COO}^-\): \[
\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{COOH} \leftrightarrow \text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{COO}^- + \text{H}^+ \tag{1}
\]

Therefore, the positive charges of the 33ATO/Ti surface at pH = 3.8 and 5.0 were favored to attract anion in the reaction solution, and the activity of ATO/Ti toward CA degradation is high. It was found by Pirilä et al. [39] that the phenolic compounds exhibited the best-degraded ability at low pH. pH higher than the PZC (6.4) catalyst surface is negatively charged, which led to a decline in the interactions between CA and 33ATO/Ti. Therefore, the photocatalytic activity decreased appreciably in pH 7.0 and 9.0. However, the dissociation of CA strongly occurred at pH = 3.8 and 5.0 while it mainly existed in neutral molecules at pH = 3.0, because the formation of radicals was reduced in a strongly acidic medium [40]. Consequently, the catalytic activity was low at pH = 3.0. The same result was obtained in the study of Zhang et al. [41]. The optimal pH for CA conversion was discovered to be at pH = 3.8.

The effect of the airflow rate on the photooxidation efficiency of CA was shown in Figure 10(c). The CA conversion reached the highest value at an airflow rate of 0.3 Lmin\(^{-1}\). As the absence of oxygen or the low concentration of oxygen, there was a decrease in CA degradation compared to the
introduction of 0.3 L min\(^{-1}\). However, the decrease of the CA efficiency was observed at the airflow rate of 0.5 L min\(^{-1}\). As a result, CA conversion only reached 68.3% at the oxygen flow rate of 0.5 L min\(^{-1}\). Similar trends were reported by Reddy et al., and oxygen acted as an electron capture agent to prevent the recombination of electrons with holes and generate strong oxidative radicals. So, the photocatalytic activity was enhanced in the optimal concentration of oxygen [42]. Besides, the hinder of the light absorbance to the catalyst occurred at the high concentration of oxygen [43]. The non-selective oxidation of the strong oxidative radicals at the high concentration of oxygen was also considered as a factor that led to the decline of pollutant degradation [44]. From the obtained results, 0.3 L min\(^{-1}\) of the airflow rate was suggested as the optimum condition for CA removal.

The recyclability of the 33ATO/Ti catalyst in the operational parameters as the catalyst dosage of 0.75 g L\(^{-1}\), the initial pH of 3.8, and the airflow rate of 0.3 L min\(^{-1}\) was measured for 90 min at continuous cycles. As can be seen in Figure 11, a gradual decline in CA degradation was after each run. After 6 cycles, the removal efficiency of CA decreased by 35%, namely, 85.1% in the first cycle and 55.7% in the sixth cycle. The reduction of the 33ATO/Ti photocatalytic activity may be explained by the precipitation of the catalyst. As a result, active sites on the surface were covered by the CA degraded sediments [37]. Furthermore, the loss of catalyst in the accumulation to eliminate CA from the mixture reaction for the next cycles was considered a certain reason for the decrease in the CA conversion [45]. The initial catalyst was 0.1875 g while the amount of the 33ATO/Ti catalyst after 6 cycles remained 0.1465 g. It should be noted that the recovery and reuse of the ATO/Ti hybrid catalyst are much easier than the powder TiO\(_2\) which has a low density. It is also an advantage of the ATO/Ti composite.

Figure 12 illustrates the 60-minute removal efficiency of CA of the catalysts: ATO, 33ATO/Ti, and TiO\(_2\) (w). Compared with ATO and TiO\(_2\) (w), the photooxidation capability was increased significantly with the catalyst of 33ATO/Ti. The hybrid catalyst systematically provided the highest CA efficiency with 77.1%, almost twice of ATO (30.4%) and higher than that of TiO\(_2\) (67.1%). There was an unpredicted increase in the specific surface area of 33ATO/Ti (209.3 m\(^2\)g\(^{-1}\)) in comparison with ATO (18.1 m\(^2\)g\(^{-1}\)) and TiO\(_2\) (13.8 m\(^2\)g\(^{-1}\)). Moreover, the combination of ATO with TiO\(_2\) (w) led to a significant reduction of the bandgap energy. The bandgap energy of the 33ATO/Ti, ATO, and TiO\(_2\) (w) was calculated by the Tauc plot and exhibited the values of 3.06, 3.42 [22], and 3.14 eV [16], respectively. A similar conclusion was reported by Xing et al., and the introduction of NiTiO\(_3\) enhanced the photocatalytic properties of TiO\(_2\) as the surface area, light absorption, and charge separation [13]. These researches have confirmed that the particle size has an important effect on the catalyst properties. It was reported in [46] that the photocatalytic activity for the organic compounds was inversely proportional to the TiO\(_2\) nanoparticle size. As the particle size increases, the photocatalytic rate constant exponentially decreases [47]. This is related to the larger number of surface active sites and faster spatial charge transfer as the catalyst particle size decreases [48]. The dispersion of ATO into smaller particles by TiO\(_2\) (3-5 nm compared to 20 nm [22]) contributes to a reduction in the recombination of photogenerated electron-hole pair and an increase in the photocatalytic activity. However, the photocatalytic activity of the sample 33ATO/Ti was lower than that of the ATO/Ti(a), with a conversion \(X_{60}\) of 88.5% compared to 77.1%. It could be related to TiO\(_2\) phase composition in the ATO/Ti sample which is only TiO\(_2\) anatase while in the ATO/Ti(a) the anatase, the rutile phase ratio (88:12) [22] is close to the optimal value [49], and the crystal size of the anatase TiO\(_2\) in ATO/Ti was twice that of the sample ATO/Ti(a).

4. Conclusion

The heterostructured ATO/Ti catalysts have been successfully prepared by the low-temperature sol-gel method combined with the hydrothermal technique in the water medium. The resulting heterostructured ATO/Ti catalysts possessed superior properties to parents ATO and TiO\(_2\) (w).
such as small particle size, outstandingly high specific surface area, large pore volume, and low band gap energy. A catalyst with the introduction of 33% ATO reached the highest photocatalytic activity. Excellence performance of the 33ATO/Ti catalyst was associated with the improvement of the specific surface area, the reduction of band gap energy, and the presence of more hydroxyl groups on the surface. The CA degradation was favorable at its natural pH (pHCA = 3.8). At the optimal conditions, the CA removal on 33ATO/Ti catalyst was twice that on ATO and higher than that on TiO2(w).

The results confirm that the heterostructured ATO/Ti catalyst can be synthesized under mild conditions and is considered as a potential UV–photocatalyst for waste treatment.

**Data Availability**

The data used to support the findings of this study are included within the article.

**Conflicts of Interest**

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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**References**

[1] L. Célia, M. Joana, M. C. Maria, P. N. João, M. A. M. Fernanda, and V. Sandra Cabo, "A biodegradation bench study of cork wastewater using gamma radiation," *Journal of Advanced Oxidation Technologies*, vol. 19, no. 1, pp. 73–78, 2016.

[2] A. Krastanov, Z. Alexieva, and H. Yemendzhiev, "Microbial degradation of phenol and phenolic derivatives," *Engineering in Life Sciences*, vol. 13, no. 1, pp. 76–87, 2013.

[3] F. Lukmanal Hakkim, M. Miura, N. Matsuda et al., "An in vitro evidence for caffeic acid, rosmarinic acid and trans cinnamic acid as a skin protectant against γ-radiation," *International Journal of Low Radiation*, vol. 9, no. 4, pp. 305–316, 2014.

[4] S. G. Kumar and L. G. Devi, "Review on modified TiO2 photocatalysis under UV/visible light: selected results and related mechanisms on interfacial charge carrier transfer dynamics," *The Journal of Physical Chemistry A*, vol. 115, no. 46, pp. 13211–13241, 2011.

[5] W. Wang, S. Zhu, Y. Cao et al., "Edge-enriched ultrathin MoS2 embedded yolk-shell TiO2 with boosted charge transfer for superior photocatalytic H2 evolution," *Advanced Functional Materials*, vol. 29, no. 36, article 1901958, 2019.

[6] J. Shi and L. Guo, "ABO3-based photocatalysts for water splitting," *Progress in Natural Science: Materials International*, vol. 22, no. 6, pp. 592–615, 2012.

[7] P. Kanhere and Z. Chen, "A review on visible light active perovskite-based photocatalysts," *Molecules*, vol. 19, no. 12, pp. 19995–20022, 2014.

[8] K. Maeda, "Photocatalytic water splitting using semiconductor particles: history and recent developments," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 12, no. 4, pp. 237–268, 2011.

[9] C. W. Chang and C. Hu, "Graphene oxide-derived carbon-doped SrTiO3 for highly efficient photocatalytic degradation of organic pollutants under visible light irradiation," *Chemical Engineering Journal*, vol. 383, p. 123116, 2020.

[10] S. Shen, S. A. Lindley, X. Chen, and J. Z. Zhang, "Hematite heterostructures for photoelectrochemical water splitting: rational materials design and charge carrier dynamics," *Energy & Environmental Science*, vol. 9, no. 9, pp. 2744–2775, 2016.

[11] H. Barnsdøk, L. Blanco, D. Hermosilla, and Á. Blanco, "Heterogeneous photo–Fenton processes using zero valent iron microspheres for the treatment of wastewaters contaminated with 1,4-dioxane," *Chemical Engineering Journal*, vol. 284, pp. 112–121, 2016.

[12] F. Wu, Y. Yu, H. Yang et al., "Simultaneous enhancement of charge separation and hole transportation in a TiO2-SrTiO3 core-shell nanowire photoelectrochemical system," *Advanced Materials*, vol. 29, no. 28, article 1701432, 2017.

[13] C. Xing, Y. Liu, Y. Zhang et al., "Porous NiTiO3/TiO2 nanostructures for photocatalytic hydrogen evolution," *Journal of Materials Chemistry A*, vol. 7, no. 28, pp. 17053–17059, 2019.

[14] Y. Wei, J. Wang, R. Yu, J. Wan, and D. Wang, "Constructing SrTiO3–TiO2 Heterogeneous hollow multi-shelled structures for enhanced solar water splitting," *Angewandte Chemie International Edition*, vol. 58, no. 5, pp. 1422–1426, 2019.

[15] J. Huang, Y. Jiang, G. Li, C. Xue, and W. Guo, "Hetero-structural NiTiO2/TiO2 nanotubes for efficient photocatalytic hydrogen generation," *Renewable Energy*, vol. 111, pp. 410–415, 2017.

[16] D. T. Nguyen, C. A. Ha, and T. Nguyen, "Controlling phase composition, properties and activity of TiO2Nano-Photocatalyst synthesized by hydrothermal technique in the degradation of cinnamic acid solution," *Journal of Nanoscience and Nanotechnology*, vol. 20, no. 9, pp. 5418–5425, 2020.

[17] E. M. M. Ewais, N. H. A. Besisa, and A. Ahmed, "Aluminum titanate based ceramics from aluminum sludge waste," *Ceramics International*, vol. 43, no. 13, pp. 10277–10287, 2017.

[18] T. Hono, N. Inoue, M. Morimoto, and Y. Suzuki, "Reactive sintering and microstructure of uniform, openly porous Al2TiO5,?" *Journal of Asian Ceramic Societies*, vol. 1, no. 2, pp. 178–183, 2013.

[19] M. Jayasankar, S. Ananthakumar, P. Mukundan, and K. G. K. Warrier, "Low temperature synthesis of aluminum titanate by an aqueous sol–gel route," *Materials Letters*, vol. 61, no. 3, pp. 790–793, 2007.

[20] M. Sobhani, H. R. Rezaie, and R. Naghizadeh, "Sol–gel synthesis of aluminum titanate (Al2TiO5) nano-particles," *Journal of Materials Processing Technology*, vol. 206, no. 1-3, pp. 282–285, 2008.

[21] F. Bakhshandeh, A. Azarniya, H. R. Madaah Hosseini, and S. Jafari, "Are aluminium titanate-based nanostructures new photocatalytic materials? Possibilities and perspectives," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 353, pp. 316–324, 2018.

[22] D. T. Nguyen, C. A. Ha, T. Nguyen, H. P. Phan, and T. C. Hoang, "A low temperature fabrication and photocactivity of Al2TiO5 in cinnamic acid degradation," *Materials Transactions*, vol. 60, no. 9, pp. 2022–2027, 2019.

[23] D. Afouxenidis, R. Mazzocco, G. Vourlias et al., "ZnO-based thin film transistors employing aluminum titanate gate..."
dielectrics deposited by spray pyrolysis at ambient air,” *ACS Applied Materials & Interfaces*, vol. 7, no. 13, pp. 7334–7341, 2015.

[24] E. N. Bakatula, D. Richard, C. M. Neculita, and G. J. Zagury, “Determination of point of zero charge of natural organic materials,” *Environmental Science and Pollution Research*, vol. 25, no. 8, pp. 7823–7833, 2018.

[25] D. T. Nguyen, C. A. Ha, and T. Nguyen, “Fabrication of TiO$_2$/Al$_2$TiO$_5$ nanocomposite photocatalysts,” *International Journal of Nanotechnology*, vol. 17, no. 7-10, pp. 607–622, 2020.

[26] D. Chen, Q. Hao, Z. Wang, H. Ding, and Y. Zhu, “Influence of phase structure and morphology on the photocatalytic activity of bismuth molybdates,” *CrystEngComm*, vol. 18, no. 11, pp. 1976–1986, 2016.

[27] D. Li, H. Song, X. Meng et al., “Effects of particle size on the structure and photocatalytic performance by alkali-treated TiO$_2$,” *Nanomaterials*, vol. 10, no. 3, p. 546, 2020.

[28] K. Y. Jung and S. B. Park, “Effect of calcination temperature and addition of silica, zirconia, alumina on the photocatalytic activity of titania,” *Korean Journal of Chemical Engineering*, vol. 18, no. 6, pp. 879–888, 2001.

[29] Y. Jiang, H. Ning, C. Tian et al., “Single-crystal TiO$_2$ nanorods assembly for efficient and stable cocatalyst-free photocatalytic hydrogen evolution,” *Applied Catalysis B: Environmental*, vol. 229, pp. 1–7, 2018.

[30] D. H. Wang, L. Jia, X. L. Wu, L. Q. Lu, and A. W. Xu, “One-step hydrothermal synthesis of N-doped TiO$_2$/C nanocomposites with high visible light photocatalytic activity,” *Nanoscale*, vol. 4, no. 2, pp. 576–584, 2012.

[31] B. L. Mojet, S. D. Ebbesen, and L. Lefferts, ”Light at the interface: the potential of attenuated total reflection infrared spectroscopy for understanding heterogeneous catalysis in water,” *Chemical Society Reviews*, vol. 39, no. 12, pp. 4643–4655, 2010.

[32] M. Wan, W. Li, Y. Long, and Y. Tu, “Electrochemical determination of tryptophan based on Si-doped nano-TiO$_2$ modified glassy carbon electrode,” *Analytical Methods*, vol. 4, no. 9, pp. 2860–2865, 2012.

[33] J. Lee, Z. Li, L. Zhu, S. Xie, and X. Cui, “Ti$_{3+}$ self-doped TiO$_2$ via facile catalytic reduction over Al(acac)$_3$ with enhanced photoelectrochemical and photocatalytic activities,” *Applied Catalysis B: Environmental*, vol. 224, pp. 715–724, 2018.

[34] W. Dong, Y. Yao, L. Li et al., “Three-dimensional interconnected mesoporous anatase TiO$_2$ exhibiting unique photocatalytic performances,” *Applied Catalysis B: Environmental*, vol. 217, pp. 293–302, 2017.

[35] A. Azarniya, M. Zekavat, M. Soltaninejad et al., “Preparation of nitrogen-doped aluminium titanate (Al$_x$Ti$_{3-x}$O$_7$) nanostructures: application to removal of organic pollutants from aqueous media,” *Advanced Powder Technology*, vol. 31, no. 8, pp. 3328–3341, 2020.

[36] M. Jamil, Z. S. Khan, A. Ali, and N. Iqbal, “Studies on solution processed Graphene- Nb$_2$O$_5$ nanocomposite based photoanode for dye-sensitized solar cells,” *Journal of Alloys and Compounds*, vol. 694, pp. 401–407, 2017.

[37] B. Kakavandi, A. Takdastan, S. Pourfadakari, M. Ahmadmoazzam, and S. Jorfi, “Heterogeneous catalytic degradation of organic compounds using nanoscale zero-valent iron supported on kaolinite: Mechanism, kinetic and feasibility studies,” *Journal of the Taiwan Institute of Chemical Engineers*, vol. 96, pp. 329–340, 2019.

[38] V. Simon, A. Thuret, L. Candy et al., “Recovery of hydroxycinnamic acids from renewable resources by adsorption on zeolites,” *Chemical Engineering Journal*, vol. 280, pp. 748–754, 2015.

[39] M. Piriä, M. Saouabe, S. Ojala et al., “Photocatalytic degradation of organic pollutants in wastewater,” *Topics in Catalysis*, vol. 58, no. 14–17, pp. 1085–1099, 2015.

[40] J. Madureira, L. Barros, R. Melo, S. Cabo Verde, I. C. F. R. Ferreira, and F. M. A. Maragaça, “Degradation of phenolic acids by gamma radiation as model compounds of cork wastewaters,” *Chemical Engineering Journal*, vol. 341, pp. 227–237, 2018.

[41] G. Zhang, Q. Wang, W. Zhang, T. Li, Y. Yuan, and P. Wang, “Effects of organic acids and initial solution pH on photocatalytic degradation of bisphenol a (BPA) in a photo-Fenton-like process using goethite (α-FeOOH),” *Photochemical & Photobiological Sciences*, vol. 15, no. 8, pp. 1046–1053, 2016.

[42] C. V. Reddy, B. Babu, I. N. Reddy, and J. Shim, “Synthesis and characterization of pure tetragonal ZrO$_2$ nanoparticles with enhanced photocatalytic activity,” *Ceramics International*, vol. 44, no. 6, pp. 6940–6948, 2018.

[43] S. M. Lam, J. C. Sin, and A. R. Mohamed, “Parameter effect on photocatalytic degradation of phenol using TiO$_2$-P25/activated carbon (AC),” *Korean Journal of Chemical Engineering*, vol. 27, no. 4, pp. 1109–1116, 2010.

[44] C. Wang, D. Wu, P. Wang, Y. Ao, J. Hou, and J. Qian, “Effect of oxygen vacancy on enhanced photocatalytic activity of reduced ZnO nanorod arrays,” *Applied Surface Science*, vol. 325, pp. 112–116, 2015.

[45] H. Rezaei-Vahidian, A. R. Zarei, and A. R. Soleymani, "Degradation of nitro-aromatic explosives using recyclable magnetic photocatalyst: catalyst synthesis and process optimization,” *Journal of Hazardous Materials*, vol. 325, pp. 310–318, 2017.

[46] M. Strauss, M. Pastorello, F. A. Sigoli, J. M. de Souza e Silva, and I. O. Mazali, "Singular effect of crystallite size on the charge carrier generation and photocatalytic activity of nano-TiO$_2$,” *Applied Surface Science*, vol. 319, pp. 151–157, 2014.

[47] H. Lin, C. P. Huang, W. Li, C. Ni, S. I. Shah, and Y. H. Tseng, "Size dependency of nanocrystalline TiO$_2$ on its optical property and photocatalytic reactivity exemplified by 2-chlorophenol," *Applied Catalysis B: Environmental*, vol. 68, no. 1-2, pp. 1–11, 2006.

[48] H. Cheng, W. Wang, B. Huang et al., "Tailoring AgI nanoparticles for the assembly of AgI/BiOI hierarchical hybrids with size-dependent photocatalytic activities," *Journal of Materials Chemistry A*, vol. 1, no. 24, pp. 7131–7136, 2013.

[49] T. Ohno, K. Sarukawa, T. Tokkieda, and M. Matsumura, "Morphology of a TiO$_2$ photocatalyst (Degussa, P-25) consisting of anatase and rutile crystalline phases," *Journal of Catalysis*, vol. 203, no. 1, pp. 82–86, 2001.