Research Article

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

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In this work, heterostructured catalyst $\text{Al}_2\text{TiO}_5/\text{TiO}_2$ (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 ($\text{TiO}_2(\text{w})$) as well as Al_2TiO_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 $\text{TiO}_2(\text{w})$ and ATO. The factors as the catalyst dosage (C_{cat}), the airflow rate (Q_{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 $C_{\text{cat}} = 0.75 \text{ gL}^{-1}$, $Q_{\text{air}} = 0.3 \text{ Lmin}^{-1}$, and $\text{pH} = 3.8$. The highest 60-minute removal efficiency of CA reached 77.1% on 33ATO/Ti compared with 67.1% and 30.4% on $\text{TiO}_2(\text{w})$ 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 concentra-

tion [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 environmentally 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 photostability 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 CO_2 or NO_x 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 $\text{TiO}_2/\text{SrTiO}_3$ 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 $\text{SrTiO}_3\text{-TiO}_2$ boosted the separation efficiency of the photogenerated charge carriers [14]. Also, the porous $\text{NiTiO}_3/\text{TiO}_2$ 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 NiTiO_3 was an effective cocatalyst, which improved the photocatalytic activity of TiO_2 on the heterostructural $\text{NiTiO}_3/\text{TiO}_2$ 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 TiO_2 depend on the synthetic environment. A remarkable result indicated that the point of zero charge (PZC) value of the produced TiO_2 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 TiO_2 in different media.

The aluminum titanate Al_2TiO_5 (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, Al_2TiO_5 has been recognized as an innovative material for photodegradation in wastewater treatment. However, in most studies [19–21], Al_2TiO_5 was synthesized by the sol-gel method at high temperature ($>900^\circ\text{C}$). 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 TiO_2 and commercial P25 TiO_2 [22]. The combination of ATO and TiO_2 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 Al_2TiO_5 (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) isopropoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$, 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 $y\text{ATO/Ti}$, 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 K_α radiation and recorded in $2\theta = 10 - 80^\circ$. 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 JEOL 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 mgL^{-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 LZ1-00 U600 lamps ($\lambda \approx 350 - 400 \text{ nm}$, 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 ($C_{\text{cat}} = 0.50, 0.75, 1.00$, and 1.25 gL^{-1}), the initial pH solution (pH = 3.0, 3.8, 5.0, 7.0, and 9.0), and the supply airflow rate ($Q_{\text{air}} = 0, 0.1, 0.3$, and 0.5 Lmin^{-1}) was surveyed. The recyclability of catalysts was tested at the optimized conditions until CA conversion at the end of the reaction batch reduced to around 30% compared to the first batch. CA solution 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 $2\theta = 25.2^\circ$. Other phases of TiO_2 such as rutile or brookite were not observed on the samples. Furthermore, diffraction peaks at 2θ 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 $\text{TiO}_2(\text{w})$ sample only contained the anatase phase, while the $\text{TiO}_2(\text{a})$ 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 $\text{TiO}_2(\text{w})$, 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 chargers [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 $2\theta = 25.2^\circ$ and $2\theta = 26.6^\circ$, 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 peaks. Meanwhile, the B_{1g} peak assigned to the symmetric bending vibration of O-Ti-O, and the A_{1g} peak was the anti-symmetric 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 $2900\text{--}3700 \text{ cm}^{-1}$ 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 $400\text{--}800 \text{ cm}^{-1}$ [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 catalysts 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. FESEM image shows that ATO exists in the form of large blocks ranging in size between 50 and 500 nm (Figure 3(a)), while $\text{TiO}_2(\text{w})$ exists in sphere-like particles of 5–10 nm size [11] assembling into large blocks (Figure 3(b)). As a result, these two materials exhibit low specific surface areas, $18.1 \text{ m}^2\text{g}^{-1}$ for ATO [22] and $13.8 \text{ m}^2\text{g}^{-1}$ for $\text{TiO}_2(\text{w})$ [16]. The hybrid material ATO/Ti has a completely different morphology. As can be seen from FESEM images of ATO/Ti samples, there are two types of particles with different morphologies. The thin square-shaped particles of size were $100 \text{ nm} \times 100 \text{ nm} \times 3 \text{ nm}$, and quasisphere-like particles are several nm in

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

TABLE 1: The crystalline size of the TiO_2 anatase at $2\theta = 25.2^\circ$ (d_{Ti}) and Al_2TiO_5 at $2\theta = 26.6^\circ$ (d_{ATO}) from the XRD pattern; the specific surface area (S_{BET}), the pore volume (V_{pore}), and the pore size (d_{pore}) from BET adsorption isotherm, the bandgap energy (E_{G}), and absorption wavelength (λ) from UV-Vis diffuse reflectance spectra of the ATO/Ti catalysts.

Catalyst	d_{Ti} (nm)	d_{ATO} (nm)	S_{BET} (m^2g^{-1})	V_{pore} (mLg^{-1})	d_{pore} (nm)	E_{G} (eV)	λ (nm)
ATO [22]	—	33.6	18.1	—	2.80	3.42	430
$\text{TiO}_2(\text{w})$ [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 2: FTIR spectra of ATO/Ti catalysts.

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 TiO_2 , 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 TiO_2 . The inset in Figure 4 showed that the (101) plane of the anatase TiO_2 established the majority in the structure of TiO_2 with the d -spacing of 0.35 nm. From the SEM and HRTEM images, it can be seen that TiO_2 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 $\text{TiO}_2(\text{w})$, 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 ($56\text{-}93\text{ m}^2\text{g}^{-1}$) [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_{BET}) of the ATO/Ti hybrid material depends on its composition. The specific surface area increased from $18.1\text{ m}^2\text{g}^{-1}$ to $135.1\text{ m}^2\text{g}^{-1}$ when the ATO content increased from 0% to 25% and reached the maximum value of $209.3\text{ m}^2\text{g}^{-1}$ 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 TiO_2

FIGURE 3: FESEM images of the samples: (a) ATO, (b) TiO₂(w), (c) 25ATO/Ti, (d) 33ATO/Ti, and (e) 50ATO/Ti.

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

FIGURE 4: HRTEM images of the catalysts: (a, b) ATO and (c, d) 33ATO/Ti.

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 TiO₂ 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 TiO₂ 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 TiO₂ square-shaped plates as seen in the HR-TEM image, resulting in Ti element enrichment on the surface.

Figure 6 depicts N₂ adsorption-desorption isotherms of the 33ATO/Ti catalyst. The N₂ adsorption-desorption isotherms of the *as*-prepared 33ATO/Ti nanocomposites exhib-

ited 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), TiO₂ (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 Al₂TiO₅ with TiO₂ formed new bonds to vary the bandgap

FIGURE 5: EDS mapping and EDX spectrum of the catalysts: (a) TiO₂(w), (b) ATO, and (c) 33ATO/Ti.

TABLE 2: The element composition from the EDX spectrum.

Catalyst	Weight (%)		
	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

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 TiO₂(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 TiO₂ cages as seen in the FESEM image (Figure 3). It was observed that the breakdown of the order structure of TiO₂ 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.

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: TiO₂(w), ATO, 25ATO/Ti, 33ATO/Ti, and 50ATO/Ti.

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

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

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°C.

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

FIGURE 10: Effects of the conditions of the photocatalytic degradation of CA conversion on the 33ATO/Ti catalyst at $T = 25^{\circ}\text{C}$. (a) The effect of the catalyst dosage ($\text{pH} = 3.8$, $Q_{\text{air}} = 0.3 \text{ Lmin}^{-1}$), (b) the initial pH solution ($C_{\text{cat}} = 0.75 \text{ gL}^{-1}$, $Q_{\text{air}} = 0.3 \text{ Lmin}^{-1}$), and (c) the airflow rate ($\text{pH} = 3.8$, $C_{\text{cat}} = 0.75 \text{ gL}^{-1}$).

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 pK_a value (4.44) [38], CA was deprotonated to form anion $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{COO}^-$:

Therefore, the positive charges of the 33ATO/Ti surface at pH = 3.8 and 5.0 were favored to attract anion in the reac-

tion 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

FIGURE 11: The recyclability of the 33ATO/Ti catalyst for CA degradation.

introduction of 0.3 Lmin^{-1} . However, the decrease of the CA efficiency was observed at the airflow rate of 0.5 Lmin^{-1} . As a result, CA conversion only reached 68.3% at the oxygen flow rate of 0.5 Lmin^{-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 Lmin^{-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 gL^{-1} , the initial pH of 3.8, and the airflow rate of 0.3 Lmin^{-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 $\text{TiO}_2(\text{w})$. Compared with ATO and $\text{TiO}_2(\text{w})$, 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

FIGURE 12: The 60 min CA removal efficiency in photocatalytic reaction on catalysts: ATO, 33ATO/Ti, and $\text{TiO}_2(\text{w})$ at $C_{\text{cat}} = 0.75 \text{ gL}^{-1}$, $Q_{\text{air}} = 0.3 \text{ Lmin}^{-1}$, and $T = 25^\circ\text{C}$.

higher than that of $\text{TiO}_2(\text{w})$ (67.1%). There was an unpredicted increase in the specific surface area of 33ATO/Ti ($209.3 \text{ m}^2\text{g}^{-1}$) in comparison with ATO ($18.1 \text{ m}^2\text{g}^{-1}$) and $\text{TiO}_2(\text{w})$ ($13.8 \text{ m}^2\text{g}^{-1}$). Moreover, the combination of ATO with $\text{TiO}_2(\text{w})$ led to a significant reduction of the bandgap energy. The bandgap energy of the 33ATO/Ti, ATO, and $\text{TiO}_2(\text{w})$ 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 $\text{TiO}_2(\text{w})$

such as small particle size, outstandingly high specific surface area, large pore volume, and low bandgap 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 bandgap energy, and the presence of more hydroxyl groups on the surface. The CA degradation was favorable at its natural pH ($\text{pH}_{\text{CA}} = 3.8$). At the optimal conditions, the CA removal on 33ATO/Ti catalyst was twice that on ATO and higher than that on $\text{TiO}_2(\text{w})$. 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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