

Article

Facile Synthesis of Potassium-Doped Titanium Oxide Nanostructure (K₂TiO₅)/AlO(OH) Composites for Enhanced Photocatalytic Performance

So Yoon Lee ¹, Tatsuya Matsubara ¹, Daiki Numata ² and Ai Serizawa ^{1,*} 

¹ Department of Materials Science and Engineering, College of Engineering, Shibaura Institute of Technology, Toyosu, Koto-ku, Tokyo 135-8548, Japan; soyoon@shibaura-it.ac.jp (S.Y.L.); ac16082@shibaura-it.ac.jp (T.M.)

² Graduate School of Engineering and Science, Shibaura Institute of Technology, Toyosu, Koto-ku, Tokyo 135-8548, Japan; ac15058@shibaura-it.ac.jp

* Correspondence: serizawa@shibaura-it.ac.jp

Abstract: Generally, nanoparticles (NPs) are used as photocatalysts, which sometimes results in difficulties in the separation and recycling of photocatalysts from suspensions after their application in water and wastewater treatment, which hinders industrial applications of NPs that are too fine to be removed by gravitational settling. This can be solved by using support NPs to overcome these problems. -OH enrich AlO(OH), which is produced by a steam coating process, has been could be used as a possible support, because the -OH groups on the surface can interact with foreign molecules; thus, various composite functional materials can be prepared. Potassium doped titanium oxide NPs, which are produced by a wet corrosion process, namely K₂TiO₅, have been selected as photocatalysts, because K₂TiO₅ have sufficient K⁺ ions, thereby expecting the chemical bonding with -OH group from AlO(OH). This study fabricated a novel photocatalysis system made by combining K₂TiO₅ as catalysts and AlO(OH) as the catalysts' support, namely K₂TiO₅/AlO(OH) composites. The K₂TiO₅ nanowires, obtained from 10 mol/L of a KOH solution treated with Ti and AlO(OH) at 280 °C for 24 h through a steam coating process, yielded the highest surface area and the highest photocatalytic performance.

Keywords: photocatalysis; AlOOH; K₂TiO₅; coating; WCP



Citation: Lee, S.Y.; Matsubara, T.; Numata, D.; Serizawa, A. Facile Synthesis of Potassium-Doped Titanium Oxide Nanostructure (K₂TiO₅)/AlO(OH) Composites for Enhanced Photocatalytic Performance. *Catalysts* **2021**, *11*, 548. <https://doi.org/10.3390/catal11050548>

Academic Editors: Leonarda Francesca Liotta, Abel Santos and Wenfeng Shanguan

Received: 16 August 2020

Accepted: 23 April 2021

Published: 25 April 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The optical and electrical properties and catalytic performance of materials strongly depend on their morphology and structure. The high quality of nanostructures with controlled crystalline, grain, and surface architectures is of great fundamental and technological interest because of their promising new properties, which can be valuable for advanced materials [1–8]. In particular, the hierarchical self-assembly of nanoscale materials (e.g., particles, cluster, wires, belts, sheets, and tubes) into novel architectures of a higher dimensionality is highly desirable because these structures could have new properties that can be meaningful for the fabrication of advanced nanodevices and in other nanotechnology applications [9,10]. Several researchers have studied the optical and electrical properties and catalytic performances of materials using different semiconductors, including single catalysts like TiO₂ and ZrO₂; double catalysts, like Cu–Fe/TiO₂–SiO₂, and Cu–ZnO/Pt–K₂Ti₆O₁₃; and metal and compound oxides, such as CuO, LaCoO₃, Ga₂O₃, and ATaO₃, where A represents Na, Li, and K [11–17].

Titanium oxide (TiO_x) materials have attracted considerable interest in many fields of research, including the fields of photovoltaic and photocatalysis [18–21]. In particular, the photocatalysis of a TiO_x semiconductor has been actively studied and applied in environmental decontamination, such as air purification, water disinfection, hazardous waste remediation, and water purification, because of its biological and chemical inertness,

strong oxidizing power, cost effectiveness, and long-term stability against photocorrosion and chemical corrosion [22–26]. The TiO_2 group is composed of rutile, anatase, and brookite, and their band gap is around 3.2 eV [19,23,27–30]. In particular, nanostructured alkali metal incorporated titanates containing A–Ti–O (A indicates alkali element and/or H) bonds have been produced as nanotubes, nanorods, nanofibers, and nanosheets.

They have attracted considerable interest because of their unique layered structure. Among them, potassium (K)-incorporated TiO_2 is of particular interest because of its specific photochemical properties and artificial cage type structure. Although these K-incorporated nanostructured titanium oxides films (nTOFs) have been one of the leaders in this new class of materials, their synthesis still has limitations to tackle [2]. So far, there is plenty of research into enhancing the photocatalytic activity; one effective way of doing this is to minimize particle size [2,31,32]. Generally, particles are used as photocatalysts, and nanoscale particles present some difficulties in the separation and recycling of photocatalysts from suspensions after their application in water and wastewater treatment, which hinders industrial applications of TiO_2 nanoparticles that are too fine to be removed by gravitational settling because of the strong Brownian motion [33,34]. In order to overcome these problems, structures that can contain nanoscale particles have been considered.

Herein, aluminum (Al)-based materials are considered attractive because of their ultra-lightness, cost effectiveness, and so on. Generally, Al-based materials have superior mechanical and physical properties, making them ideal for use as structural materials. These properties include a high strength-to-weight ratio, good formability, high thermal conductivity, and excellent recyclability. In this way, Al-based materials have been used for numerous applications in a wide range of industries, including automobiles, building, and heat-transfer components [35,36].

Among them, boehmite ($\gamma\text{-AlO}(\text{OH})$) is one of the most important materials and has attracted a lot of attention [37]. Generally, $\text{AlO}(\text{OH})$ has many advantages, such as a high resistance, cost effectiveness, and diversity of fabrication for various morphologies. In particular, the most significant property is the following: as $\text{AlO}(\text{OH})$ has a large number of -OH groups on the surface, $\text{AlO}(\text{OH})$ is inclined to interact with foreign molecules, and thus various functional composite materials can be prepared [38,39].

Based on these material properties, $\text{AlO}(\text{OH})$ has the potential to be a support for nanoparticles. In order to use it with high-quality Ti-based catalysts, potassium-doped titanium oxide nanoparticles, namely KTiO_x s, are suitable as counter materials, because KTiO_x s have sufficient K^+ ions, thereby enabling chemical bonding with the -OH group from $\text{AlO}(\text{OH})$. In our previous research, KTiO_x s nanowires could be obtained on a metal surface through a wet corrosion process (WCP) [2,40]. WCP relies on potassium hydroxide (KOH) treatment of Ti metals, and has demonstrated a high efficiency and high reproducibility in producing a nanostructured surface with a high surface area and with varying potassium doping. The produced KTiO_x s nanowires showed high photocatalytic performances [2,40]. WCP is a simple one-step green synthesis method done at room-temperature without any supplementary treatments. The formation of KTiO_x s nanowires is directly affected by the solution concentration, which also changes the K content in the nanostructures formed on the surface. Simultaneously, the surface area and photocatalytic activity scales can be changed with the KOH concentration. Thus, WCP is a promising method for the efficient and well-tunable production of KTiO_x s nanowires as catalysts.

In order to synthesize $\text{AlO}(\text{OH})$ as a support for catalysts, recently, a steam coating process has been created to produce $\text{AlO}(\text{OH})$ [41,42]. Generally, the steam coating process allows for producing a dense film on the surface of a metal using the reaction of Al with water, which is synthesized by a pressure such as an autoclave. Note that the steam coating process uses only water; therefore, this is a simple and eco-friendly method to synthesize the oxide layer. The oxide layer can be grown directly on a substrate, so that the oxide layer exhibits excellent adhesion to the substrate. Furthermore, the process can be applied to components with complicated shapes and large substrates. In addition, the steam coating process does not require any pre-treatment, and so the fabrication step can be reduced.

AlO(OH) is one of the main hydroxide layers synthesized through this process. It is another big challenge to apply this method for photocatalyst support.

This study aimed to fabricate a novel photocatalyst system made using a combination of KTiO_xs as the catalyst and AlO(OH) as the catalyst support, namely $\text{KTiO}_x\text{s}/\text{AlO(OH)}$ composites, in order to easily separate them from their suspension after their application in water and wastewater treatment. In addition, this study systematically investigated the best optimized conditions for photocatalysis within this system using various conditions of $\text{KTiO}_x\text{s}/\text{AlO(OH)}$ composites.

2. Results and Discussions

Figure 1 shows the FE-SEM images of the surfaces of the Al substrates after a steam coating process at 180 °C and 280 °C for 24 h. A thin film was clearly observed on the surface after applying the steam coating process at 180 °C for 24 h (Figure 1a). However, a crystallized thick film was observed on the surface after being subjected to a steam coating process at 280 °C for 24 h (Figure 1b). Both of the films fully covered the surface, and the distribution of the crystal size was small, regardless of the process conditions. The average length and width of the crystals of the thin film was $< 220 \pm 80$ nm and $< 20 \pm 30$ nm, respectively, while the average length and width of the lath-like crystal of thick film was $< 650 \pm 75$ nm and $< 65 \pm 30$ nm, respectively. Note that these values were calculated using $n = 20$ within the FE-SEM images. It is worthwhile that both the length and width can be controlled spontaneously according to the steam coating process temperature.

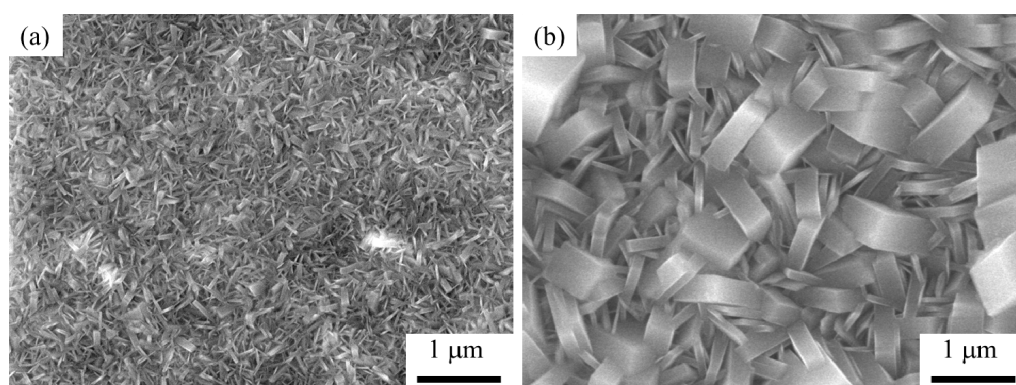
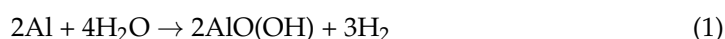


Figure 1. FE-SEM images of specimens subjected to steam coating process under different conditions: (a) 180 °C for 24 h and (b) 280 °C for 24 h.

Figure 2 shows the XRD profiles of the obtained AlO(OH) films that were prepared through the steam coating process at 180 °C and 280 °C for 24 h. Several peaks corresponding to aluminum hydroxide, including AlO(OH), were observed in all of the specimens. Compared with the AlO(OH) film that was prepared at 180 °C for 24 h, the crystallinity of the AlO(OH) film that was prepared at 280 °C for 24 h was higher.

It can be explained that this phenomenon is the reaction that balanced the water and Al during the chemical reaction of the steam coating process. The chemical reaction between Al and water likely occurs as follows.



It has been reported that AlO(OH) is at its most stable form from around 280 °C [43]. The reaction environment of the steam coating process was balanced by subcritical water in the liquid phase and saturated steam in the gas phase. Note that the state water is presented in a general pressure–temperature diagram. Subcritical water exists at temperatures between the atmospheric boiling point and the critical temperature of water. Therefore, the most impactful chemical reaction happens through the formation of AlO(OH). Here, this is worthwhile, because the large number of -OH groups on the surface were induced by

this reaction, which are expected to interact with foreign molecules in order to fabricate a variety of composite functional materials. Therefore, the steam coating process condition can be completed through this reaction for this work.

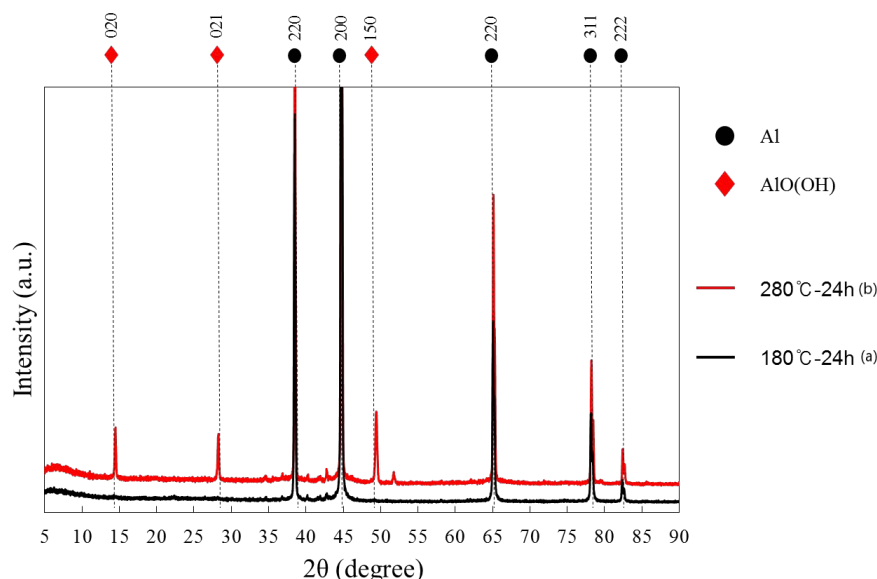


Figure 2. XRD pattern of specimens subjected to a steam coating process under different condition: (a) 180 °C for 24 h and (b) 280 °C for 24 h.

Figure 3 shows the surface area of the obtained the AlO(OH) crystals that were prepared at 180 °C and 280 °C for 24 h by AFM. Figure 3a shows the 3D images of the obtained AlO(OH) surfaces. After the steam coating process, synthesized crystals are clearly observed compared with the untreated sample. Based on this observation, a high surface area could be achieved by applying a steam coating process at 280 °C for 24 h, because the microstructures of the lath crystals have a bumpy geometry, which could increase the surface area (Figure 3b). So, we can conclude that a high temperature treatment condition for the steam coating process can increase the surface area.

From here, we would like to demonstrate the results of KTiO_xs nanowires as photocatalysts. Figure 4 shows the FE-SEM and TEM images of the KTiO_xs nanowires obtained by WCP. Compared with the untreated sample, unique nanowires were observed on the surface of the Ti particles after WCP, as in previous works [2,40]. The initial Ti materials were 200 µm in size. After KOH treatment, the nanowires were synthesized on the Ti surface, and each of the nanowires were around 200 nm in size. Based on these results, it can be confirmed that Ti particles can successfully modify nanostructures through WCP. Figure 4d shows a TEM image of the KTiO_x nanowires with a diameter in the range of 10–30 nm. The presence of K in the individual KTiO_x nanowires was confirmed by STEM-based EDX mapping. A quantitative analysis yielded a K-concentration of about 45±11 wt.%.

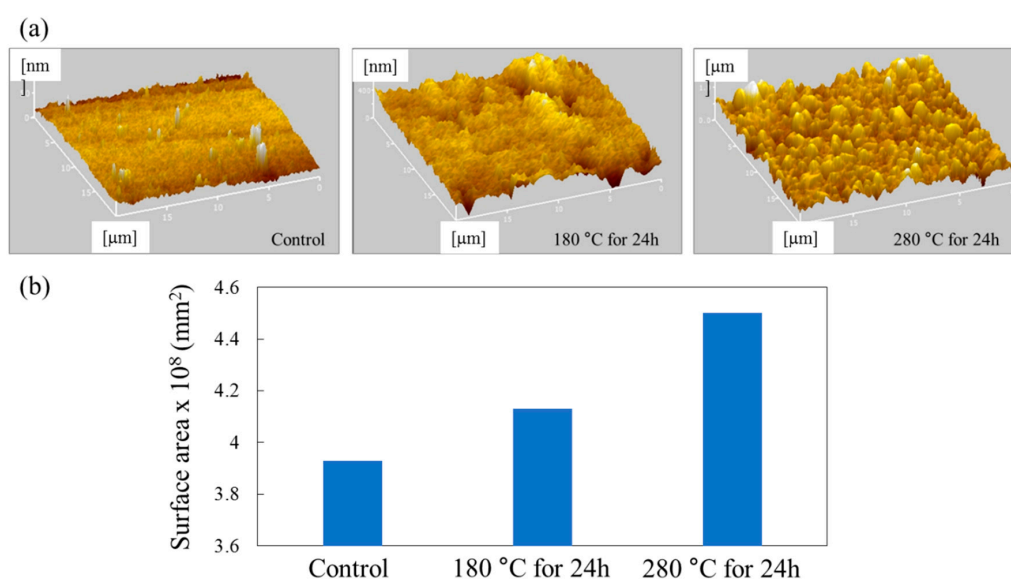


Figure 3. AFM observations of the surface area of specimens after the steam coating process under different condition: (a) the 3D images of each of the specimens for the control and for those subjected to steam coating under different conditions of 180 °C for 24h and 280 °C for 24h. (b) The results of surface areas for each of the specimens.

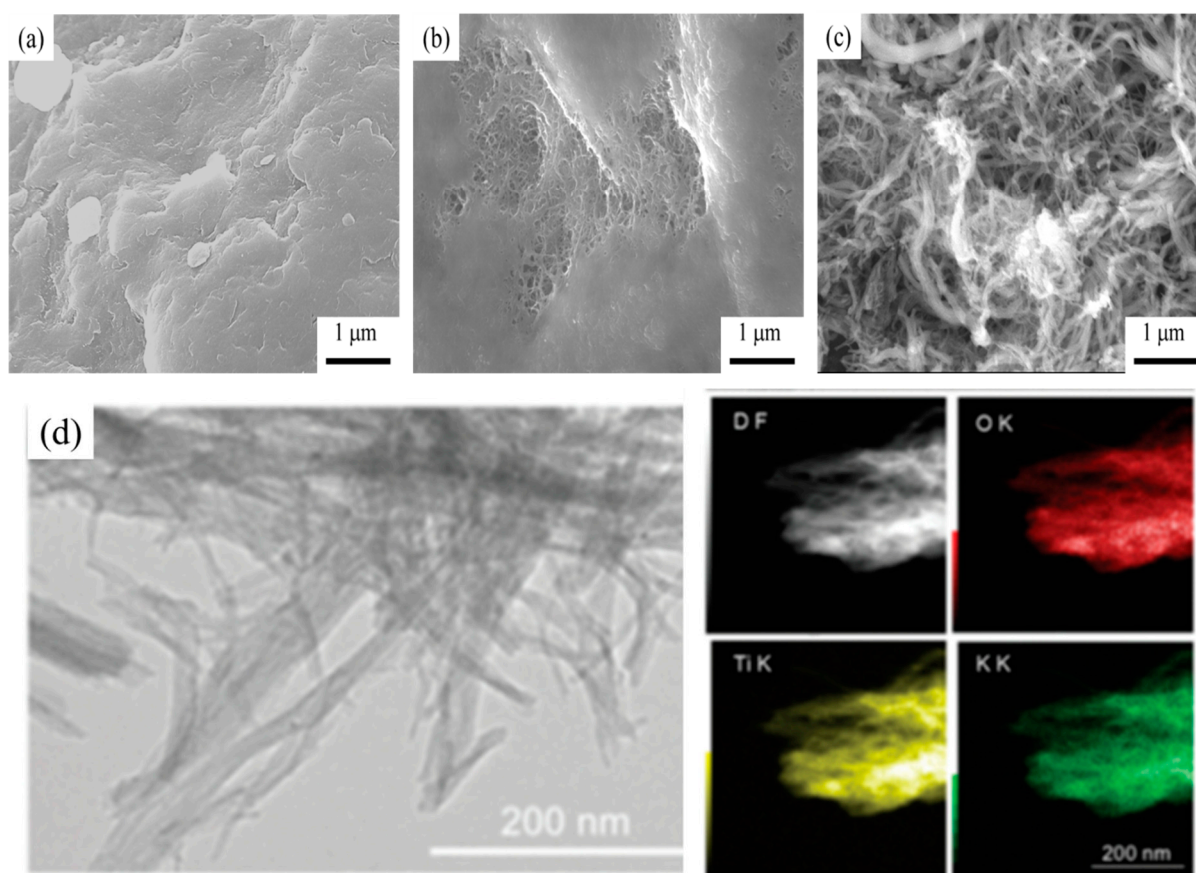


Figure 4. FE-SEM images of the specimens subjected to a wet corrosion process under different conditions: (a) control, (b) 1 mol/L-KOH solution treated Ti for 24h, (c) 10 mol/L-KOH solution treated Ti for 24h, and (d) TEM image of KTiO_xS nanowires present in the outer shell area of the Ti particles. The dark-field STEM image (DF) and the EDX maps (O-, K-, and Ti-maps) taken from the nanowires indicate the presence of KTiO_xS.

The Raman spectra of the obtained KTiO_xs nanowires are presented in Figure 5. New peaks were observed for the potassium titanate phase (280 cm^{-1}), namely KTiO_xs , caused mainly by the structural changes in TiO_2 [44,45]. The synthesis of the KTiO_xs involved the rearrangement of the Ti–O bonds. Potassium atoms were inserted in the space between the Ti–O bonds. The Ti–O–K bonds were formed with some of the broken Ti–O bonds; the other Ti–O bonds were reserved. The peaks at 445 , 660 , and 903 cm^{-1} were assigned to different TiO_2 phases (anatase, rutile, and brookite) [45,46]. Therefore, this indicates that KTiO_xs exhibited the characteristics of a (Ti–O–K) structure unit containing TiO_2 phases [45]. A Raman spectroscopy with back-scattering configuration was used for examining the structural properties of the films. Raman shifts are affected by the vibration of the electronic polarization of the constituents in the films, which depend on bonding characteristics such as the atomic distance and bonding angle [47]. Therefore, the structure of the product changed when the chemical bond was rearranged. In order to verify the surface chemical composition of the obtained nanostructured oxide films, an X-ray photoelectron spectroscopy (XPS) analysis was performed. The incorporation of K into titanium oxide films could be evidenced by the existence of the K2p peak in the XPS spectrum. The XPS result (Figure 6) shows that the peak of the K element was observed at about 293.5 eV , which was the region of the compound for K^+ [2].

Therefore, these results can be expected to make a chemical bonding with -OH group from $\text{AlO}(\text{OH})$. The Raman results confirmed that the amount and crystallinity of the obtained KTiO_xs nanowires increased at a high concentration for the KOH solution. This result may explain the generation of more chemical bonding between OH^- and K^+ for suitable composites for photocatalysis.

Figures 7 and 8 show the FE-SEM images and EDX analysis of the obtained $\text{KTiO}_x\text{s}/\text{AlO}(\text{OH})$ composites. In the case of the KTiO_xs obtained from the 1 mol/L-KOH treatment, it is hard to see the combination of KTiO_xs and $\text{AlO}(\text{OH})$; however, the composites formed with KTiO_xs obtained from the 10 mol/L-KOH treatment are clearly observed. It can be assumed that the K^+ ion site has less 1 mol/L-KOH treated Ti compared with the 10 mol/L-KOH treated Ti, based on the Raman results. Unique nanowires of KTiO_xs were observed so, it can be said that this composite was of a combination of KTiO_xs and $\text{AlO}(\text{OH})$. In detail, an EDX analysis was carried out to confirm this composite. The Ti component is clearly shown in the EDX mapping analysis, indicating that $\text{KTiO}_x\text{s}/\text{AlO}(\text{OH})$ composites were successfully obtained during the reaction (Figure 8).

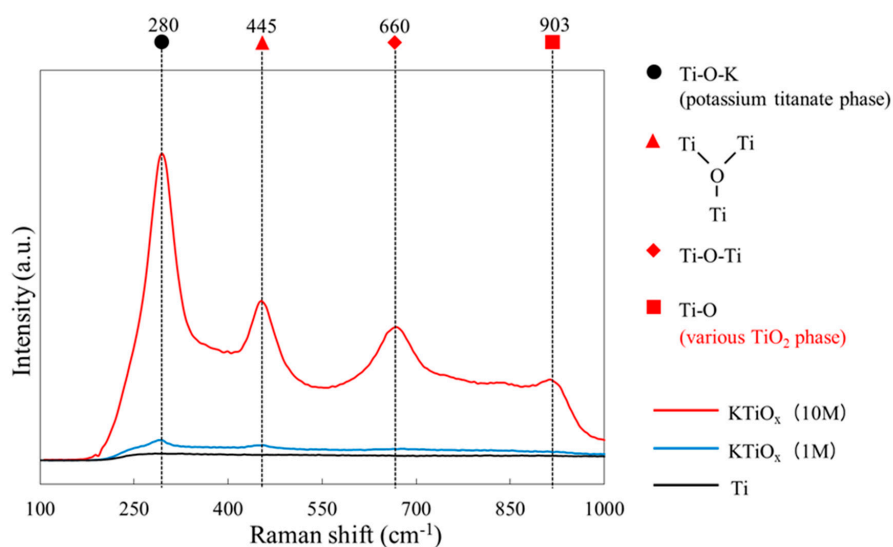


Figure 5. Raman profile of after the wet corrosion process (WCP) process.

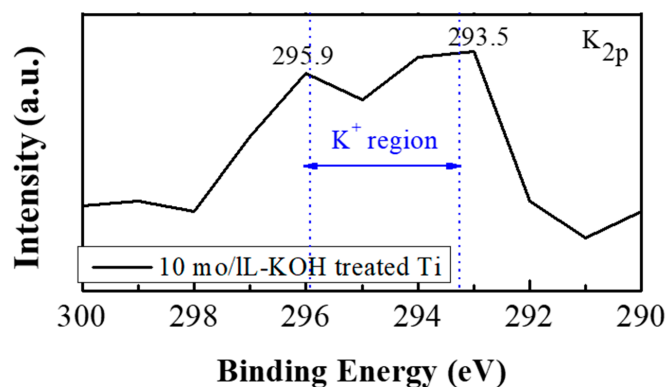


Figure 6. K2p XPS spectra of the surface of the 10 mol/L-KOH treated Ti.

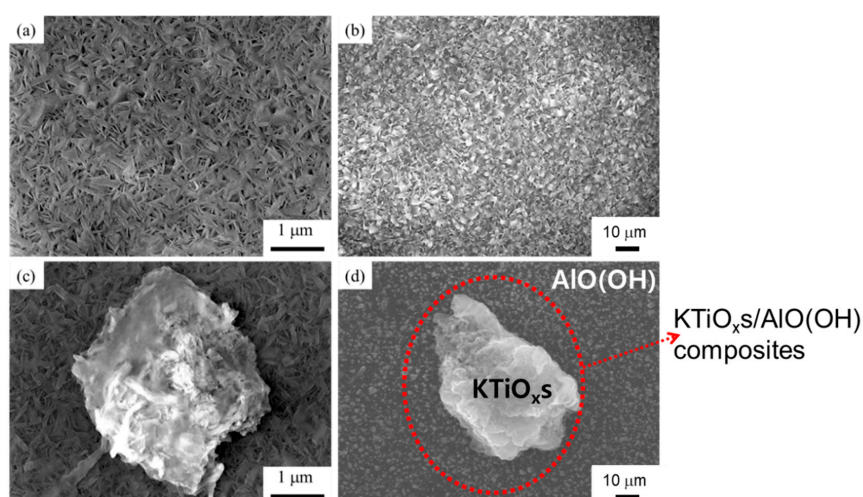


Figure 7. FE-SEM images of the specimens after synthesizing the $\text{KTiO}_x\text{s}/\text{AlO}(\text{OH})$ composites with different conditions: Note that the sample names of composites are given as the conditions of WCP to produce the KTiO_xs and the conditions of the steam coating process to produce $\text{AlO}(\text{OH})$: (a) 1 mol/L-KOH solution/180 °C for 24 h, (b) 1 mol/L-KOH solution/280 °C for 24 h, (c) 10 mol/L-KOH solution /180 °C for 24 h, and (d) 10 mol/L-KOH solution/280 °C for 24 h.

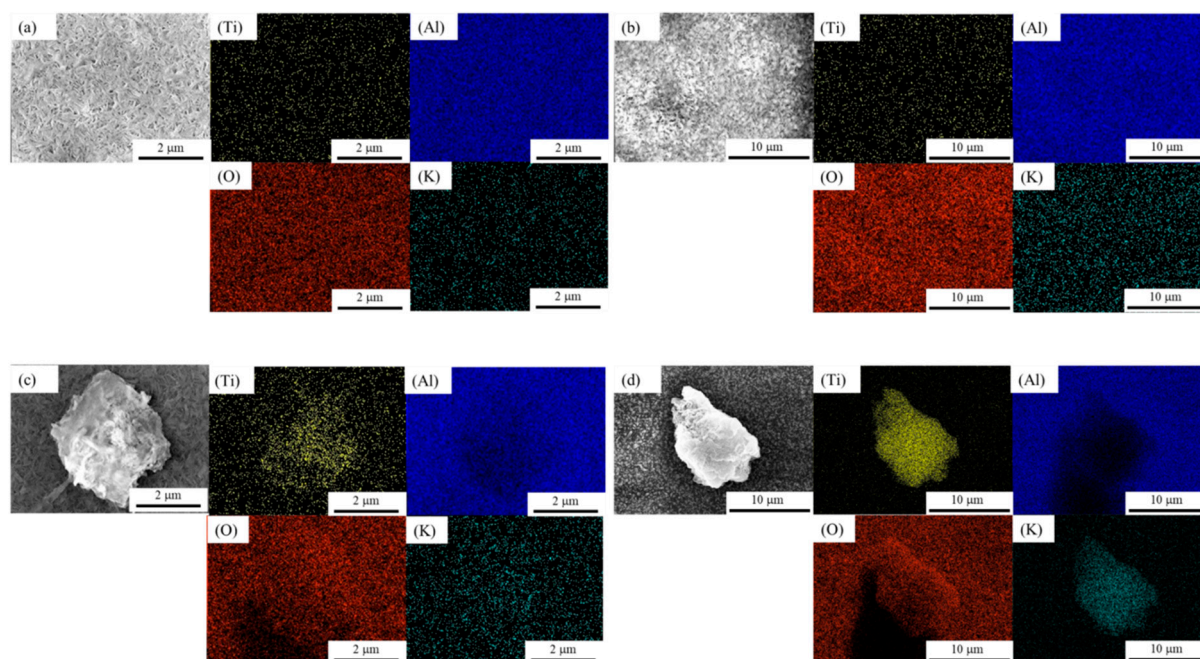


Figure 8. EDX analysis of each sample with element mapping. Note that the sample names of the composites are given as the conditions of WCP to produce the KTiO_xs and the conditions of the steam coating process to produce $\text{AlO}(\text{OH})$: (a) 1 mol/L-KOH solution/180 °C for 24 h, (b) 1 mol/L-KOH solution/280 °C for 24 h, (c) 10 mol/L-KOH solution/180 °C for 24 h, and (d) 10 mol/L-KOH solution/280 °C for 24 h.

In order to figure out the chemical bonding of the $\text{KTiO}_x\text{s}/\text{AlO}(\text{OH})$ composites obtained here, FTIR was carried out (Figure 9). The strong band at $3000\text{--}3400\text{ cm}^{-1}$ and the weak band at $1600\text{--}1700\text{ cm}^{-1}$ can be assigned to the stretching and bending modes of the adsorbed water [48]. Other absorption peaks were observed at around $480\text{--}500\text{ cm}^{-1}$ after the steam coating process, which could be attributed to Al-O symmetric stretching and ring vibration mode in Al-O tetraheda formed through the oxygen atom [49]. In particular, the $\text{KTiO}_x\text{s}/\text{AlO}(\text{OH})$ composite revealed the stretching vibration mode of Ti-O (580 cm^{-1}) and Ti-O-Ti (720 cm^{-1}) with Al-O bonding [50]. On the basis of these results, K^+ from KTiO_xs and the -OH group from $\text{AlO}(\text{OH})$ could undergo chemical bonding to fabricate the composite. Therefore, it can be assumed that the initial concept to make the composite using $\text{AlO}(\text{OH})$ as a support for KTiO_xs is successfully achieved.

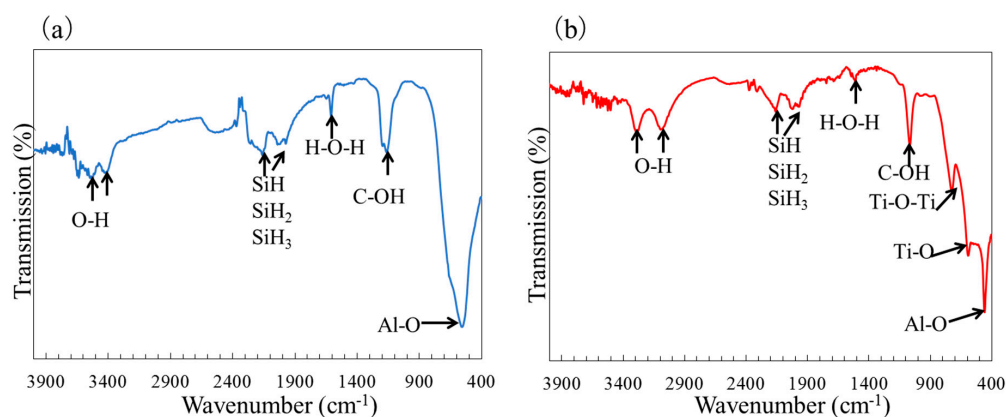


Figure 9. FTIR spectrum of the prepared substrates before/after synthesizing the $\text{KTiO}_x\text{s}/\text{AlO}(\text{OH})$ composites: Note that the sample names of the composites are given as the conditions of WCP to produce the KTiO_xs and the conditions of steam coating process to produce $\text{AlO}(\text{OH})$: (a) bare $\text{AlO}(\text{OH})$ prepared at 280 °C for 24 h and (b) 10 mol/L-KOH solution treated Ti at 280 °C for 24 h.

In order to examine the photocatalytic activity of the obtained KTiO_x s nanowires, the photodegradation of methylene blue (MB) was evaluated under UV light irradiation. The band gap of the obtained KTiO_x s is around 2.8–2.9 eV. The UV–VIS absorption spectra presented in Figure 10A demonstrate the decomposition of MB dye, leading to decolorization. For comparison, the absorption spectra of the untreated sample are also presented. The major absorption peaks appeared at about 612 and 664 nm, which is characteristic for MB dye [51]. The major absorption peaks appeared and were used as a direct indication of photocatalytically activated dye degradation. Indeed, all of the obtained KTiO_x s specimens showed a higher photocatalytic activity than the untreated samples. This observation was in agreement with the remarkable photocatalytic properties reported for nanostructured titanium oxide materials with an enhanced surface area and increased electron transfer ability [2,52]. Interestingly, the 10 mol/L-KOH-treated Ti specimen showed a higher photocatalytic activity than the 1 mol/L-KOH-treated Ti. The intensity of the MB peaks of the 10 mol/L-KOH treated Ti decreased to a blank level after 30 min of UV exposure. The degradation rate of the 10 mol/L-KOH treated Ti was almost 99% in this study. This result is superior to the reported results (high score of the reported results was 90%) [29,53,54]. Generally, the photocatalytic activity leading to the degradation of dyes depends on the catalyst concentration. The high surface area exerts a synergistic effect on the catalyst concentration. As the higher catalyst concentration creates an increase in adsorbed dye molecules, and a higher photocatalytic performance can be expected [55].

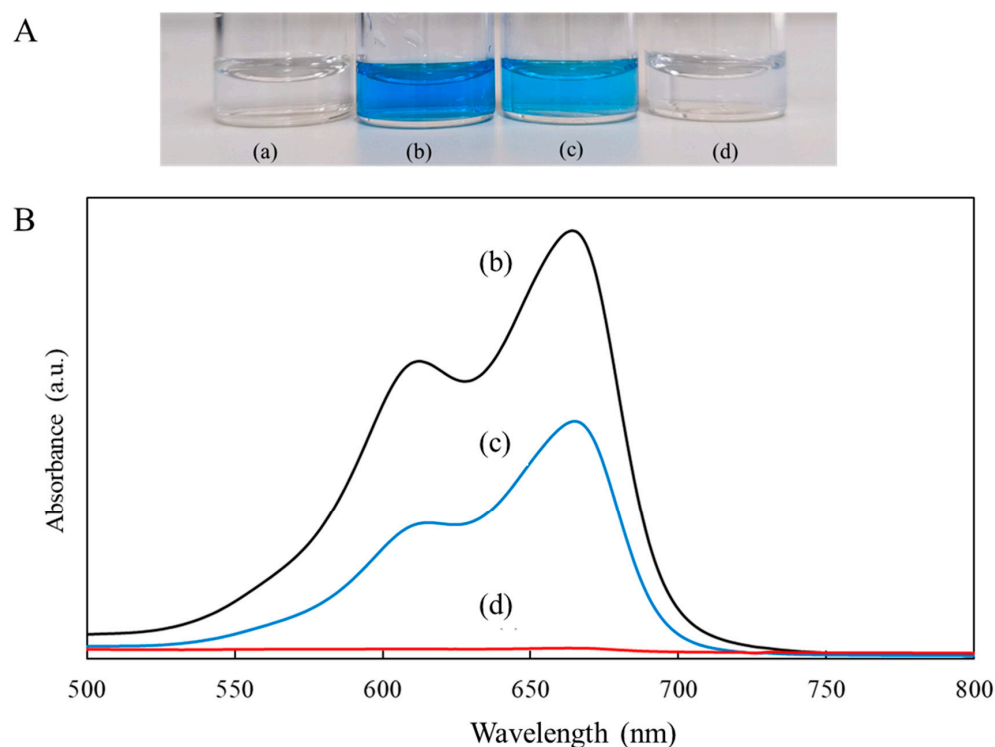


Figure 10. (A) Photographs and (B) UV–VIS absorption spectra from the original MB dye, and from the dye exposed to UV light irradiation for 30 min: (a) pure H_2O , (b) original MB, (c) 1 mol/L-KOH treated Ti, and (d) 10 mol/L-KOH treated Ti.

Normally, the photocatalytic process is based on the photogeneration of electron-hole pairs, which will initiate redox reactions with the species adsorbed on the surface of the catalysts. In the photocatalytic process, OH radicals originating from the oxidation of OH^- or H_2O through the photogenerated electron-hole pairs in the presence of oxygen have been considered as the major reactants responsible for the photocatalytic oxidation of organic materials and the degradation of pollutants [22,23,56]. Consequently, improved electronic properties can be linked to an enhanced photocatalytic activity. In our work, the electronic

properties are governed by the amount of Ti–O–K components. From these results, we can conclude that an efficient charge/energy transfer occurs in the KOH-treated samples under photo-irradiation and leads to an improved photocatalytic activity, as evidenced by the drastic diminishment of the UV absorption peaks. These results clearly demonstrate that KTiO_x can be a cost-effective, highly efficient, and environmental-friendly photocatalyst.

In order to optimize the best composite conditions for the photocatalytic effect, we prepared four different KTiO_xs/AlO(OH) composites, as shown in Figure 11. For comparison, the absorption spectra of bare AlO(OH) specimens prepared by a steam coating process at 180 °C and 280 °C for 24 h were also presented as the control samples. From the results, at first, we can confirm that the KTiO_xs/AlO(OH) composites showed a higher photocatalytic activity compared with the bare AlO(OH) specimens because of the existence of KTiO_xs. Among the KTiO_xs/AlO(OH) composites, the 10 mol/L-KOH treated Ti and the steam coating AlO(OH) composite treated at 280 °C for 24 h showed a remarkable enhanced photocatalytic activity because both the KTiO_xs and AlO(OH) had a high surface area. Once again, we assume that a high surface area executes a synergistic effect on the catalyst concentration, because a large amount of dye molecules can be loaded on the surface, resulting in a higher photocatalytic performance [57,58].

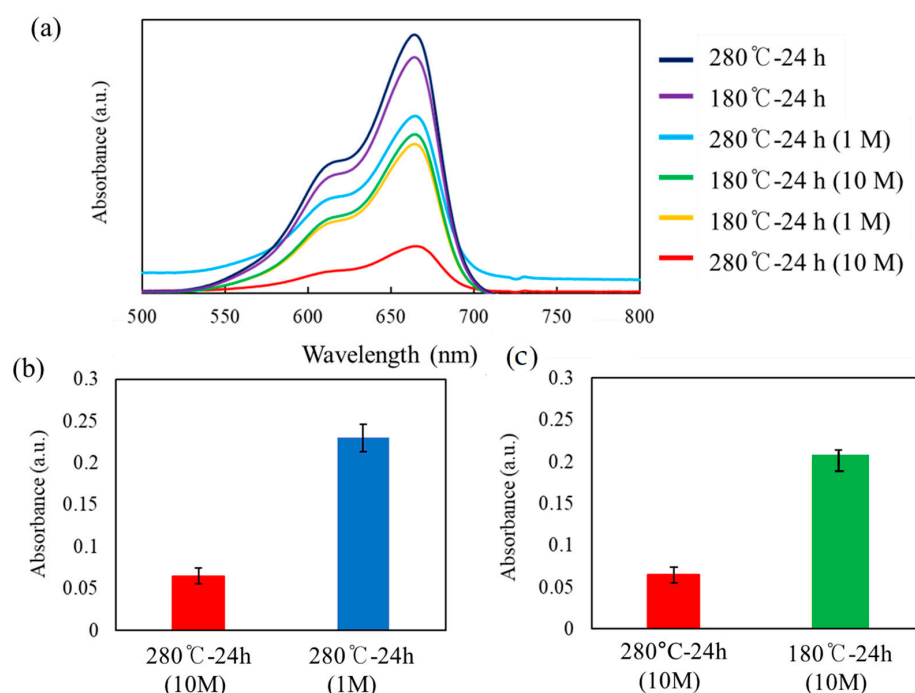


Figure 11. Analysis of the photocatalytic activity: (a) UV–VIS absorption spectra took from the original MB dye, and from the dye exposed to various conditions of KTiO_x/AlO(OH) composites after UV light irradiation for 2 h. (b) Effect of photocatalysis depends on the surface area of the KTiO_x photocatalysts. (c) Effect of photocatalysis depends on the surface area of AlO(OH).

In order to optimize the best conditions for the composites, a degradation level calculated by the intensity of the MB was used in this system. The composites used in this study are listed in Table 1.

Table 1. The conditions for each of the samples in this study.

	The Condition of Produce of Al(OH)	The Condition of Produce of KTiO _x s
180 °C-24 h	180 °C for 24 h treated Al	X
280 °C-24 h	280 °C for 24 h treated Al	X
180 °C-24 h (1 M)	180 °C for 24 h treated Al	1 M-KOH treated Ti
180 °C-24 h (10 M)	180 °C for 24 h treated Al	10 M-KOH treated Ti
280 °C-24 h (1 M)	280 °C for 24 h treated Al	1 M-KOH treated Ti
280 °C-24 h (10 M)	280 °C for 24 h treated Al	1 M-KOH treated Ti

First, in order to figure out the effect of the surface area of KTiO_xs, a higher surface area of AlO(OH) substrates was used. This indicated that the degradation function of MB with 10 mol/L-KOH treated Ti was four times higher than for the 1 mol/L-KOH treated Ti (Figure 11b). From these results, it can be seen that the 10 mol/L-KOH treated Ti catalyst is suitable for a higher photocatalysis performance because of its high surface area. Second, in order to figure out the effect of the surface area of AlO(OH), we used the 10 mol/L-KOH treated Ti as a high performance photocatalyst. From this comparison, a large surface area of AlO(OH) could contain the large amounts of KTiO_xs, thereby increasing the photocatalytic activity (Figure 11c). On the basis of these results, the K⁺ from KTiO_xs and OH⁻ from AlO(OH) could create a chemical reaction to make the composite successful, and the best composite condition for the photocatalysis was to use a high surface area for KTiO_xs and AlO(OH). Briefly, it can be explained that the best condition for the KTiO_xs/AlO(OH) composite is using 10 mol/L-KOH treated Ti as a photocatalyst and steam coating processed AlOOH treated at 280 °C for 24 h as a catalyst support.

3. Materials and Methods

3.1. Preparation of KTiO_xs/AlO(OH) Composites for Photocatalysis System

An Al-Mg-Si alloy with a size of 10 mm X 10 mm was used as the substrate for synthesizing AlO(OH) as a support. The chemical composition of the Al alloy is shown in Table 2. The chemical composition is the same as that of AA6061.

Table 2. Chemical composition of the starting materials used in the present study.

Composition (wt.%)								
Al	Mg	Si	Fe	Mn	Cr	Ti	Cu	Zn
Bal.	0.8~1.2	0.4~0.81	<0.7	<0.15	0.04~0.35	<0.15	0.15~0.4	<0.25

The steam coating process was carried out with press micro reactor (MMS-100 OM-labotech) with a volume of 10 m³ using a Teflon container with a 100-mL capacity. AA6061 substrates were placed on a substrate stage, which was made of Teflon tape, 10 mL of ultra-pure water was added to the bottom of a Teflon container to produce steam. The autoclave process was carried out by heating up to 180 °C and 240 °C for 24 h, and then was cooled down naturally at room temperature.

In order to synthesize the K-incorporated Ti (KTiO_xs) as photocatalysts, Ti microspheres (purity >99.8% and diameter of 125–250 µm) were purchased from Sigma-Aldrich in Japan. The Ti particles were soaked in 5 mL KOH solution with a concentration of 1 and 10 mol/L at room temperature for 24 h. Note that this process is called as WCP. After WCP, all particles were washed with deionized water and dried. These particles contained a Ti core and a shell of KTiO_xs nanowires forming a network.

In order to synthesize the KTiO_xs/AlO(OH) composites for the photocatalysis system, the obtained the AlO(OH) substrates were attached by a carbon type on the bottom of the container (UG Yamayu, Tokyo, Japan) and mixed with 0.75g of KTiO_xs with 4 mL of H₂O at 200 rpm for 24 h with shaking. After 24 h, the samples were washed with H₂O to remove the unattached KTiO_xs. In order to figure out the effect of the surface area of KTiO_xs and

AlO(OH), we prepared four different composites as follows. The sample names of the composites were recorded in the order of the condition of KTiO_xs/AlO(OH), as follows: 1 mol/L-KOH treated Ti/180 °C for 24 h treated Al, 1 mol/L-KOH treated Ti/280 °C for 24 h treated Ti, 10 mol/L-KOH treated Ti/180 °C for 24 h treated Al, and 10 mol/L-KOH treated Ti/180 °C for 24 h treated Ti.

3.2. Evaluation of Photocatalytic Activity of KTiO_xs/AlO(OH) Composites

First, in order to evaluate the photocatalytic activity of the KTiO_xs that were treated with 1 and 10 mol/L-KOH, with treated Ti as the photocatalysts, 2g of KTiO_xs were mixed with 2 mL of methylene blue organic dye (MB; 125 mg/L) solutions. For the photocatalysis, UV irradiation (UV light; GrassyleDio RX122, Volxjapanv, Tokyo, Japan) with a 10 cm working distance was carried out for 10, 20, and 30 min. Note that the UV light can react under a 500 nm wavelength. During UV exposure, the mixtures (KTiO_xs and MB solutions) were stirred continuously. After we confirmed the activity of the KTiO_xs, the photocatalytic activity of the KTiO_xs/AlO(OH) composites were carried out. Here, 300 mL of MB dye was drop wise on the surface of KTiO_xs/AlO(OH) composites for UV irradiation for 10, 20, and 30 min.

3.3. Characterizations

Changes in the surface structure, shape, and size of the obtained AlO(OH) and KTiO_xs nanowires were observed using a field emission scanning electron microscope (FE-SEM; JSM-7610, JEOL Ltd., Tokyo, Japan), which was operated at 15 kV. The crystal phase of the obtained AlO(OH) film was identified using X-ray diffraction (XRD; Smart Lab, Rigaku, Tokyo, Japan), with Cu K radiation (40 kV, 30 mA) within a range of 5°–90° and at a scanning rate of $2\theta = 4^\circ/\text{min}$. The surface area was measured using atomic force microscopy (AFM; AFM5000, HITACHI, Tokyo, Japan) with DFM mode at $20\ \mu\text{m} \times 20\ \mu\text{m}$. A Raman spectroscope was used for examining the structural properties of the obtained KTiO_xs nanowires. A laser Raman spectrometer (NRS-5100, JASCO, Tokyo, Japan) was used within a range of 100–1500 cm^{−1} at a 532 nm laser wavelength. For the identification and visualization of the obtained KTiO_xs/AlO(OH) composites, an energy-dispersive X-ray (SEM-EDX; JSM-7610, JEOL Ltd., Tokyo, Japan) analysis was carried out at 20 kV. To investigate the structural properties of the obtained KTiO_xs/AlO(OH) composites, Fourier-transform infrared spectroscopy (FT-IR; IRAffinity-1S, Shimadzu Co., Tokyo, Japan) was performed, which was recorded within the range of 400–4000 cm^{−1}, with 20 scans at a resolution of 4 cm^{−1}. After UV irradiation, the photocatalytic activity was evaluated by collecting the UV–VIS absorption spectra (UV–VIS Spectrophotometer; V-630Bio Spectrophotometer, JASCO, Tokyo, Japan) of the solution. The degradation efficiency was recorded as the decreased absorption peak.

4. Conclusions

The preparation of KTiO_xs/AlO(OH) composites for photocatalysis was demonstrated. In order to overcome the separation after photocatalysis and water purification using particles catalysts, a support to contain the particle catalysts is needed. Herein, KTiO_xs nanoparticles were selected as the photocatalysts, because nanostructured KTiO_xs was a promising candidate for photocatalysis in previous work. Based on this concept, AlO(OH) was considered as a support, because the enriched –OH group has a higher potential to create a chemical reaction with the K⁺ from KTiO_xs. In particular, our strategic plan for this project was to enhance the photocatalytic activity as follows: (1) to make a large surface area of support to load more catalysts and (2) to make a large surface area of catalysts to enlarge the concentration of dye molecules. In this contribution, AlO(OH) as a support was prepared by a steam coating process at 180 °C and 280 °C for 24 h to fabricate the different surface areas, and the KTiO_xs nanowires were prepared using WCP with 1 and 10 mol/L-KOH solution treatments to elongate the different surface areas. The photocatalytic activity of KTiO_xs/AlO(OH) composites was successfully studied as a function of the surface

area. The KTiO_xs nanowires obtained from the 10 mol/L-KOH solution treated Ti and the $\text{AlO}(\text{OH})$ obtained from treatment at 280°C for 24 h in a steam coating process yielded the highest surface area and also the highest photocatalytic performance. It is notable that two different facile fabrication methods can be used to fabricate high potential composites such as $\text{KTiO}_x\text{s}/\text{AlO}(\text{OH})$ for high performance photocatalysis. Therefore, we believe that the $\text{KTiO}_x\text{s}/\text{AlO}(\text{OH})$ composites produced by the WCP and steam coating process have great potential for photocatalysis, but also for photovoltaics and bio- and eco-friendly devices, where a high catalytic activity and easy cleaning are required.

Author Contributions: S.Y.L. writing the paper and supervised the experiments. T.M. and D.N. conducted the experiments and A.S. supervised the all process of this research. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by JST under the Program on Open Innovation Platform with Enterprises, Research Institute and Academia (OPERA; no. 18072116), and JSPS KAKENHI, Grant-in-Aid for Scientific Research (B) (no. 19H02482).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Paul, K.K.; Giri, P.K. Shape Tailored TiO_2 Nanostructures and Their Hybrids for Advanced Energy and Environmental Applications: A Review. *J. Nanosci. Nanotechnol.* **2019**, *19*, 307–331. [\[CrossRef\]](#) [\[PubMed\]](#)
- Lee, S.Y.; Lee, C.H.; Kim, D.Y.; Locquet, J.P.; Seo, J.W. Preparation and Photocatalytic Activity of Potassium-Incorporated Titanium Oxide Nanostructures Produced by the Wet Corrosion Process Using Various Titanium Alloys. *Nanomaterials* **2015**, *5*, 1397–1417. [\[CrossRef\]](#) [\[PubMed\]](#)
- Roselin, L.S.; Juang, R.S.; Hsieh, C.T.; Sagadevan, S.; Umar, A.; Selvin, R.; Hegazy, H.H. Recent Advances and Perspectives of Carbon-Based Nanostructures as Anode Materials for Li-ion Batteries. *Materials* **2019**, *12*, 1229. [\[CrossRef\]](#)
- Zou, S.; Yang, G.; Pang, T.; Zou, M.; Liu, R.; Chen, B.; Jia, B.; Zou, B. One-step synthesis of nail-like Mn-doped CdS/CdBr_2 hetero-nanostructures for potential lasing application. *Nanotechnology* **2019**, *30*, 075605. [\[CrossRef\]](#)
- Xiao, M.; Wang, Z.; Lyu, M.; Luo, B.; Wang, S.; Liu, G.; Cheng, H.M.; Wang, L. Hollow Nanostructures for Photocatalysis: Advantages and Challenges. *Adv. Mater.* **2019**, *31*, e1801369. [\[CrossRef\]](#) [\[PubMed\]](#)
- Chen, Q.; Wu, J.; Ou, X.; Huang, B.; Almutlaq, J.; Zhumeckenov, A.A.; Guan, X.; Han, S.; Liang, L.; Yi, Z.; et al. All-inorganic perovskite nanocrystal scintillators. *Nature* **2018**, *561*, 88–93. [\[CrossRef\]](#) [\[PubMed\]](#)
- Greaney, M.F. Photocatalysis. Copper catalysis in a blue light. *Science* **2016**, *351*, 666. [\[CrossRef\]](#)
- Ghosh, I.; Ghosh, T.; Bardagi, J.I.; König, B. Reduction of aryl halides by consecutive visible light-induced electron transfer processes. *Science* **2014**, *346*, 725–728. [\[CrossRef\]](#) [\[PubMed\]](#)
- Mann, S. The Chemistry of Form. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 3392–3406. [\[CrossRef\]](#)
- Mokari, T.; Rothenberg, E.; Popov, I.; Costi, R.; Banin, U. Selective growth of metal tips onto semiconductor quantum rods and tetrapods. *Science* **2004**, *304*, 1787–1790. [\[CrossRef\]](#)
- Chen, L.; Graham, M.E.; Li, G.H.; Gentner, D.R.; Dimitrijevic, N.M.; Gray, K.A. Photoreduction of CO_2 by TiO_2 nanocomposites synthesized through reactive direct current magnetron sputter deposition. *Thin Solid Film.* **2009**, *517*, 5641–5645. [\[CrossRef\]](#)
- Kohno, Y.; Tanaka, T.; Funabiki, T.; Yoshida, S. Photoreduction of CO_2 with H_2 over ZrO_2 . A study on interaction of hydrogen with photoexcited CO_2 . *Phys. Chem. Chem. Phys.* **2000**, *2*, 2635–2639. [\[CrossRef\]](#)
- Nguyen, T.V.; Wu, J.C.S. Photoreduction of CO_2 to fuels under sunlight using optical-fiber reactor. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 864–872. [\[CrossRef\]](#)
- Guan, G.Q.; Kida, T.; Yoshida, A. Reduction of carbon dioxide with water under concentrated sunlight using photocatalyst combined with Fe-based catalyst. *Appl. Catal. B Environ.* **2003**, *41*, 387–396. [\[CrossRef\]](#)
- Qin, S.Y.; Xin, F.; Liu, Y.D.; Yin, X.H.; Ma, W. Photocatalytic reduction of CO_2 in methanol to methyl formate over $\text{CuO}-\text{TiO}_2$ composite catalysts. *J. Colloid Interface Sci.* **2011**, *356*, 257–261. [\[CrossRef\]](#) [\[PubMed\]](#)
- Jia, L.S.; Li, J.J.; Fang, W.P. Enhanced visible-light active C and Fe co-doped LaCoO_3 for reduction of carbon dioxide. *Catal. Commun.* **2009**, *11*, 87–90. [\[CrossRef\]](#)
- Xu, D.; Yang, S.; Jin, Y.; Chen, M.; Fan, W.; Luo, B.; Shi, W. Ag-Decorated ATaO_3 ($A = \text{K}, \text{Na}$) Nanocube Plasmonic Photocatalysts with Enhanced Photocatalytic Water-Splitting Properties. *Langmuir* **2015**, *31*, 9694–9699. [\[CrossRef\]](#)
- Valero, R.; Morales-Garcia, A.; Illas, F. Investigating the character of excited states in TiO_2 nanoparticles from topological descriptors: Implications for photocatalysis. *Phys. Chem. Chem. Phys.* **2020**, *22*, 3017–3029. [\[CrossRef\]](#)
- Gao, Y.; Nie, W.; Zhu, Q.; Wang, X.; Wang, S.; Fan, F.; Li, C. The Polarization Effect in Surface-Plasmon-Induced Photocatalysis on Au/TiO_2 Nanoparticles. *Angew. Chem. Int. Ed. Engl.* **2020**, *59*, 18218–18223. [\[CrossRef\]](#)

20. Murillo-Acevedo, Y.; Bernal-Sanchez, J.; Giraldo, L.; Sierra-Ramirez, R.; Moreno-Pirajan, J.C. Initial Approximation to the Design and Construction of a Photocatalysis Reactor for Phenol Degradation with TiO₂ Nanoparticles. *ACS Omega* **2019**, *4*, 19605–19613. [[CrossRef](#)] [[PubMed](#)]
21. Chattopadhyay, S.; Bysakh, S.; Mishra, P.M.; De, G. In Situ Synthesis of Mesoporous TiO₂ Nanofibers Surface-Decorated with AuAg Alloy Nanoparticles Anchored by Heterojunction Exhibiting Enhanced Solar Active Photocatalysis. *Langmuir* **2019**, *35*, 14364–14375. [[CrossRef](#)]
22. Tran, M.L.; Fu, C.C.; Juang, R.S. Removal of metronidazole and amoxicillin mixtures by UV/TiO₂ photocatalysis: An insight into degradation pathways and performance improvement. *Environ. Sci. Pollut. Res. Int.* **2019**, *26*, 11846–11855. [[CrossRef](#)]
23. Murgolo, S.; Franz, S.; Arab, H.; Bestetti, M.; Falletta, E.; Mascolo, G. Degradation of emerging organic pollutants in wastewater effluents by electrochemical photocatalysis on nanostructured TiO₂ meshes. *Water Res.* **2019**, *164*, 114920. [[CrossRef](#)] [[PubMed](#)]
24. Lu, Z.; Zhang, K.; Liu, X.; Shi, Y. High efficiency inactivation of microalgae in ballast water by a new proposed dual-wave UV-photocatalysis system (UVA/UVC-TiO₂). *Environ. Sci. Pollut. Res. Int.* **2019**, *26*, 7785–7792. [[CrossRef](#)]
25. Santhanakrishnan, H.; Mani, N.; Jayaram, A.; Suruttaiyadiy, P.; Chellamuthu, M.; Shimomura, M. Engineering of mono-dispersed mesoporous TiO₂ over 1-D nanorods for water purification under visible light irradiation. *Environ. Sci. Pollut. Res. Int.* **2021**, *28*, 18768–18777. [[CrossRef](#)]
26. Eidsvag, H.; Bentouba, S.; Vajeeston, P.; Yohi, S.; Velauthapillai, D. TiO₂ as a Photocatalyst for Water Splitting-An Experimental and Theoretical Review. *Molecules* **2021**, *26*, 1687. [[CrossRef](#)]
27. Indrakanti, V.P.; Kubicki, J.D.; Schobert, H.H. Photoinduced activation of CO₂ on Ti-based heterogeneous catalysts: Current state, chemical physics-based insights and outlook. *Energy Environ. Sci.* **2009**, *2*, 745–758. [[CrossRef](#)]
28. Li Puma, G.L.; Bono, A.; Krishnaiah, D.; Collin, J.G. Preparation of titanium dioxide photocatalyst loaded onto activated carbon support using chemical vapor deposition: A review paper. *J. Hazard. Mater.* **2008**, *157*, 209–219. [[CrossRef](#)]
29. Ait Atmane, A.; Bourouina-Bacha, S. Method for attachment of TiO₂ using design of experiments: Application to the photocatalysis of a model pollutant methylene blue dye. *Water Sci. Technol.* **2020**, *82*, 2076–2084. [[CrossRef](#)] [[PubMed](#)]
30. Murakami, Y.; Kamegawa, T.; Kobori, Y.; Tachikawa, T. TiO₂ superstructures with oriented nanospaces: A strategy for efficient and selective photocatalysis. *Nanoscale* **2020**, *12*, 6420–6428. [[CrossRef](#)]
31. Jia, H.; Wong, Y.L.; Jian, A.; Tsoi, C.C.; Wang, M.; Li, W.; Zhang, W.; Sang, S.; Zhang, X. Microfluidic Reactors for Plasmonic Photocatalysis Using Gold Nanoparticles. *Micromachines* **2019**, *10*, 869. [[CrossRef](#)] [[PubMed](#)]
32. Luo, G.; Liu, H.; Li, W.; Lyu, X. Automobile Exhaust Removal Performance of Pervious Concrete with Nano TiO₂ under Photocatalysis. *Nanomaterials* **2020**, *10*, 2088. [[CrossRef](#)]
33. Ali, S.; Li, Z.J.; Ali, W.; Zhang, Z.Q.; Wei, M.Z.; Qu, Y.; Jing, L.Q. Synthesis of Au-decorated three-phase-mixed TiO₂/phosphate modified active carbon nanocomposites as easily-recycled efficient photocatalysts for degrading high-concentration 2,4-DCP. *RSC Adv.* **2019**, *9*, 38414–38421. [[CrossRef](#)]
34. Valerio, A.; Sarria, M.P.; Rodriguez-Lorenzo, L.; Hotza, D.; Espina, B.; Gonzalez, S.Y.G. Are TiO₂ nanoparticles safe for photocatalysis in aqueous media? *Nanoscale Adv.* **2020**, *2*, 4951–4960. [[CrossRef](#)]
35. Nassoy, F.; Pinault, M.; Descarpentries, J.; Vignal, T.; Banet, P.; Coulon, P.E.; Goisard de Monsabert, T.; Hauf, H.; Aubert, P.H.; Reynaud, C.; et al. Single-Step Synthesis of Vertically Aligned Carbon Nanotube Forest on Aluminium Foils. *Nanomaterials* **2019**, *9*, 1590. [[CrossRef](#)] [[PubMed](#)]
36. Malekizadeh, A.; Schenk, P.M. High flux water purification using aluminium hydroxide hydrate gels. *Sci. Rep.* **2017**, *7*, 17437. [[CrossRef](#)]
37. Tao, W.; Zhong, H.; Pan, X.; Wang, P.; Wang, H.; Huang, L. Removal of fluoride from wastewater solution using Ce-ALOOH with oxalic acid as modification. *J. Hazard. Mater.* **2020**, *384*, 121373. [[CrossRef](#)]
38. Xu, X.; Zu, X.; Ao, D.; Yu, J.; Xiang, X.; Xie, W.; Tang, Y.; Li, S.; Fu, Y. NH₃-Sensing Mechanism Using Surface Acoustic Wave Sensor with AlO(OH) Film. *Nanomaterials* **2019**, *9*, 1732. [[CrossRef](#)]
39. Zheng, G.; Wu, C.; Wang, J.; Mo, S.; Zou, Z.; Zhou, B.; Long, F. Space-Confined Effect One-Pot Synthesis of gamma-AlO(OH)/MgAl-LDH Heterostructures with Excellent Adsorption Performance. *Nanoscale Res. Lett.* **2019**, *14*, 281. [[CrossRef](#)]
40. Lee, S.Y.; Zhang, J.; Jang, L.W.; Zhang, Z.; Guo, Y.; Salameh, S.; Kim, S.; Son, D.I.; Rangasamy, V.S.; Thayumanasundaram, S.; et al. Characterization and Photocatalytic Performance of Potassium-Doped Titanium Oxide Nanostructures Prepared via Wet Corrosion of Titanium Microspheres. *J. Nanosci. Nanotechnol.* **2019**, *19*, 366–374. [[CrossRef](#)]
41. Ishizaki, T.; Miyashita, T.; Inamura, M.; Nagashima, Y.; Serizawa, A. Effect of Al Content in the Mg-Based Alloys on the Composition and Corrosion Resistance of Composite Hydroxide Films Formed by Steam Coating. *Materials* **2019**, *12*, 1188. [[CrossRef](#)] [[PubMed](#)]
42. Serizawa, A.O.T.; Watanabe, K.; Mori, K.; Yokomizo, T.; Ishzaki, T. Formation of Anticorrosive Film for Suppressing Pitting Corrosion on Al-Mg-Si Alloy by Steam Coating. *Coatings* **2018**, *8*, 23. [[CrossRef](#)]
43. Moradi, Z.; Esmaili, M.; Almasi, H. Development and characterization of kefir—Al₂O₃ nanocomposite films: Morphological, physical and mechanical properties. *Int. J. Biol. Macromol.* **2019**, *122*, 603–609. [[CrossRef](#)] [[PubMed](#)]
44. Lee, S.Y.; Ryosuke, M.; Ishihara, K.; Takai, M. Electrical Transport Ability of Nanostructured Potassium-Doped Titanium Oxide Film. *Appl. Phys. Express* **2011**, *4*, 025803. [[CrossRef](#)]
45. Su, Y.; Balmer, M.L.; Bunker, B.C. Raman Spectroscopic Studies of Silicotitanates. *J. Phys. Chem. B* **2000**, *104*, 8160–8169. [[CrossRef](#)]

46. Sakka, S.; Miyaji, F.; Fukumi, K. Structure of binary $K_2O \cdot TiO_2$ and $Cs_2O \cdot TiO_2$ glasses. *J. Non Cryst. Solids* **1989**, *112*, 64–68. [[CrossRef](#)]
47. Ali, A.M.; Hasegawa, S. Effect of hydrogen dilution on the growth of nanocrystalline silicon films at high temperature by using plasma-enhanced chemical vapor deposition. *Thin Solid Film.* **2003**, *437*, 68–73. [[CrossRef](#)]
48. Liu, C.; Shih, K.; Gao, Y.; Li, F.; Wei, L. Dechlorinating transformation of propachlor through nucleophilic substitution by dithionite on the surface of alumina. *J. Soils Sediments* **2012**, *12*, 724–733. [[CrossRef](#)]
49. Dias, V.; Maciel, H.; Fraga, M.; Lobo, A.O.; Pessoa, R.; Marciano, F.R. Atomic Layer Deposited TiO_2 and Al_2O_3 Thin Films as Coatings for Aluminum Food Packaging Application. *Materials* **2019**, *12*, 682. [[CrossRef](#)]
50. Tarigh, G.D.; Shemirani, F.; Maz'haric, N.S. Fabrication of a reusable magnetic multi-walled carbon nanotube- TiO_2 nanocomposite by electrostatic adsorption: Enhanced photodegradation of malachite green. *RSC Adv.* **2015**, *5*, 35070–35079. [[CrossRef](#)]
51. Tu, B.; Zhao, Y.; Li, J.; Du, Q.; Mao, X.; Tang, H.; Ji, J.; Han, X.; Wang, K. Establishment of recombinase polymerase amplification assay for drug resistance gene bla_(NDM) coding metallo-beta-lactamase. *J. Hyg. Res.* **2019**, *48*, 99–108.
52. Chimmikuttanda, S.P.; Naik, A.; Akple, M.S.; Rajegowda, R.H. Hydrothermal synthesis of TiO_2 hollow spheres adorned with SnO_2 quantum dots and their efficiency in the production of methanol via photocatalysis. *Environ. Sci. Pollut. Res. Int.* **2017**, *24*, 26436–26443. [[CrossRef](#)] [[PubMed](#)]
53. Akel, S.; Boughaled, R.; Dillert, R.; El Azzouzi, M.; Bahnemann, D.W. UV/Vis Light Induced Degradation of Oxytetracycline Hydrochloride Mediated by Co- TiO_2 Nanoparticles. *Molecules* **2020**, *25*, 249. [[CrossRef](#)]
54. Ben Said, M.; Bousselmi, L.; Ghrabi, A. Monitoring of methylene blue monomers and dimers to control the bacteriological water quality including application to photocatalysis. *Environ. Sci. Pollut. Res. Int* **2021**, *28*, 15819–15827. [[CrossRef](#)] [[PubMed](#)]
55. Yoko, T.; Hu, L.; Kozuka, H.; Sakka, S. Photoelectrochemical properties of TiO_2 coating films prepared using different solvents by the sol-gel method. *Thin Solid Film.* **1996**, *283*, 188–195. [[CrossRef](#)]
56. Karagoz, S.; Kiremitler, N.B.; Sakir, M.; Salem, S.; Onses, M.S.; Sahmetlioglu, E.; Ceylan, A.; Yilmaz, E. Synthesis of Ag and TiO_2 modified polycaprolactone electrospun nanofibers (PCL/ TiO_2 -Ag NFs) as a multifunctional material for SERS, photocatalysis and antibacterial applications. *Ecotoxicol. Environ. Saf.* **2020**, *188*, 109856. [[CrossRef](#)] [[PubMed](#)]
57. Moon, J.T.; Lee, S.K.; Joo, J.B. Controllable one-pot synthesis of uniform colloidal TiO_2 particles in a mixed solvent solution for photocatalysis. *Beilstein J. Nanotechnol.* **2018**, *9*, 1715–1727. [[CrossRef](#)]
58. Cao, Y.Q.; Zhao, X.R.; Chen, J.; Zhang, W.; Li, M.; Zhu, L.; Zhang, X.J.; Wu, D.; Li, A.D. TiO_xNy Modified TiO_2 Powders Prepared by Plasma Enhanced Atomic Layer Deposition for Highly Visible Light Photocatalysis. *Sci. Rep.* **2018**, *8*, 1. [[CrossRef](#)]