Annealing Temperature-Dependent Effects of Fe-Loading on the Visible Light-Driven Photocatalytic Activity of Rutile TiO$_2$ Nanoparticles and Their Applicability for Air Purification

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Received: 29 May 2020; Accepted: 1 July 2020; Published: 3 July 2020

Abstract: Commercial rutile TiO$_2$ particles (200–300 nm) were modified by the temperature-regulated chemical vapor deposition (tr-CVD) of Fe-oxide and subsequent annealing at various temperatures (300–750 °C). As a result of the modification, the photocatalytic activity of the TiO$_2$ regarding acetaldehyde removal under visible light was enhanced, and the enhancement effects were dependent on the annealing temperature. Specifically, the enhancement effects of the modification were most pronounced when Fe-TiO$_2$ was annealed at 375 °C, whereas the effects were significantly reduced by annealing at higher temperatures (525 and 750 °C). The analytical results with various techniques, including two surface-sensitive methods (XPS (X-ray photoelectron spectroscopy) and TOF-SIMS (time of flight-secondary ion mass spectrometry)), revealed that the stronger metal support interaction between TiO$_2$ and the loaded Fe-oxide at high temperature (>375 °C) resulted in the decreased charge separation efficiency and photocatalytic activity of the Fe-TiO$_2$ under light irradiation. The production scale for the Fe-TiO$_2$ photocatalysts can be easily increased (from 200 g to 8 kg per the unit process) by upsizing the reactor volume. The mass-produced samples exhibited similar activity to the samples produced at small scale, and they were photocatalytically active after being spread on a cement block (stainless steel plate) using a surface hardening agent (paint), showing the high applicability in real applications.

Keywords: iron oxide; rutile TiO$_2$; visible light-responsive photocatalyst; acetaldehyde

1. Introduction

The photocatalytic removal of harmful organic compounds in either the aqueous or gas phase has been studied extensively [1–6]. When the surface of a semiconductor is exposed to light whose energy exceeds the band gap of the semiconductor, electron-hole pairs can be generated upon the absorption of the light energy by the semiconductor. The light-induced electron-hole pairs can interact with O$_2$ and H$_2$O molecules at the surface of the semiconductor, generating strong oxidizing agents such as O$_2^-$ and OH radicals, respectively. These oxidizing agents can interact with other organic compounds on the surface, oxidizing them into less harmful species, e.g., CO$_2$ and H$_2$O, by total oxidation.

Acetaldehyde is in the class of volatile organic compounds (VOCs) that have been blamed for adverse effects on human health [7–11]. The photocatalytic removal of acetaldehyde using semiconducting materials has been studied by many research groups [12–15]. Among semiconducting...
materials, anatase TiO$_2$ has been the most popular choice as a photocatalyst due to its non-toxicity, high chemical stability, and photocatalytic activity [16–19]. However, anatase TiO$_2$ can be used effectively as a photocatalyst only under UV light but not under visible light, due to its wide band gap (~3.2 eV). The portions of UV light in sunlight at the surface of the earth and in light from indoor lamps are limited. Thus, the wide band gap of anatase TiO$_2$ hampers its applicability as a photocatalyst for indoor and outdoor air purification.

The modification of TiO$_2$ with non-metal or metal ion doping has been investigated very extensively by many research groups to develop visible-light-responsive photocatalysts based on TiO$_2$ [20–24]. The loaded dopant can provide additional electronic states between the original band gap of TiO$_2$ so that the modified TiO$_2$ can utilize visible light to generate light-induced electron-hole pairs that can initiate the photocatalytic process. It is a general belief that rutile TiO$_2$ is less advantageous than anatase TiO$_2$ due to the shorter lifetime of its induced electron-hole pairs. However, rutile TiO$_2$ exhibits a smaller band gap (~3.0 eV) than anatase TiO$_2$, which makes rutile TiO$_2$ a possible candidate base material for developing visible-light-responsive photocatalysts [25–27]. Recently, we demonstrated that the anatase-to-rutile phase transition of commercial TiO$_2$ particles (P25, Evonik), which originally consisted of both anatase and rutile phases in an 8:2 ratio, could enhance the photocatalytic activity regarding acetaldehyde oxidation under visible light irradiation [28]. The anatase-to-rutile transformation was achieved by thermal annealing at 750 °C, and the visible-light response of the rutile TiO$_2$ can be further enhanced by the small loading of Fe-oxide via the temperature-regulated chemical vapor deposition (tr-CVD) [28]. Previous results also showed that the amount of Fe-loading was an important factor in determining the photocatalytic activity of Fe-loaded rutile TiO$_2$ under visible light, since the formation of larger Fe-oxide particles on the surface of TiO$_2$ can facilitate the non-radiative recombination of light-induced electron-hole pairs [28].

In this work, we investigated the annealing temperature dependency of the enhancement effects of a small Fe-loading (0.4 wt%) on the photocatalytic activity of rutile TiO$_2$ towards acetaldehyde removal under visible light irradiation. Commercially available alumina-coated rutile TiO$_2$ particles (200–300 nm) produced via a sulfuric acid process and commonly used as a pigment in coloring processes were chosen as a starting material for the modification. These TiO$_2$ particles are widely used due to their high refractive index, giving a high hiding power in white paints, and also as UV-protection agents in various composite materials; however, these TiO$_2$ particles are known to have very little photocatalytic activity. It is notable that these TiO$_2$ materials are well known to be cost-effective, so giving photocatalytic activity to these commercially available rutile TiO$_2$ materials with a slight surface modification would accelerate the wide application of photocatalysts. A very small amount of Fe-oxide (0.4 wt%) was loaded on the rutile TiO$_2$, and the Fe-loaded TiO$_2$ particles were annealed at various temperatures in the range of 300–750 °C. We found that there was an optimum temperature (375 °C) of annealing for the maximization of the enhancement effects of Fe-loading. Various analyses, including by two surface sensitive techniques (XPS (X-ray photoelectron spectroscopy) and TOF-SIMS (time of flight-secondary ion mass spectrometry)), revealed that the stronger metal support interaction between TiO$_2$ and the loaded Fe-oxide at higher temperature (>375 °C) can reduce the charge separation efficiency and the photocatalytic activity of Fe-loaded rutile TiO$_2$ under light irradiation. In addition, the feasibility of the mass production of Fe-modified rutile TiO$_2$ and its applicability in outdoor and indoor air purification were also examined.

2. Results and Discussion

2.1. Characterization

The amount of Fe-loading in TiO$_2$ particles was determined to be 0.4 wt% by ICP-OES analysis. Figure 1a–c show TEM images of three samples (TiO$_2$, and Fe-TiO$_2$-375 and -750). In all three cases, the TiO$_2$ particles were hexagonal in shape, with a size range of 200–300 nm. Any changes in the structure of the TiO$_2$ particles upon Fe-loading and annealing were not noticeable in the TEM images,
which can be attributed to the very small amount of Fe-loading (0.4 wt%) on the TiO₂ particles. The crystallinities of all the synthesized samples (Fe-TiO₂-300, -375, -450, -525, and -750) were examined by obtaining their XRD patterns. Figure 1d shows the XRD patterns of three samples (TiO₂, and Fe-TiO₂-375 and -750) and pristine TiO₂ (a comparison of the XRD patterns of all the synthesized samples and pristine TiO₂ can be found in Supporting information). All the XRD patterns were almost identical to those of pristine TiO₂ and were well matched with the standard rutile phase TiO₂ spectrum (JCPDS No. 88-1174), and other peaks related to anatase or brookite TiO₂ were not observed. This indicated that no phase transformations of TiO₂ took place, and the loading amount of Fe was too small to be detected in the XRD analysis.

![TEM images](image-url)

**Figure 1.** Characterization results for TiO₂, Fe-TiO₂-375, and Fe-TiO₂-750 particles. TEM images of (a) TiO₂, (b) Fe-TiO₂-375, and (c) Fe-TiO₂-750 particles. (d) XRD patterns of TiO₂, Fe-TiO₂-375, and Fe-TiO₂-750 particles (XRD patterns of all the synthesized samples are provided in Supporting information).

The specific Brunauer–Emmett–Teller (BET) surface areas of all the synthesized samples and pristine TiO₂ were examined (Supporting information), and Table 1 shows the specific BET surface areas of three samples (TiO₂, and Fe-TiO₂-375 and -750). The surface area of TiO₂ gradually decreased as the annealing temperature was increased from 375 to 750 °C after Fe-loading. However, only a marginal decrease in the surface area of the TiO₂ was observed (from 15.1 to 11.8 m²/g), even after the 750 °C annealing following the Fe-loading.
Table 1. The specific Brunauer–Emmett–Teller (BET) surface areas of TiO$_2$, Fe-TiO$_2$-375, and Fe-TiO$_2$-750 particles (the specific BET surface areas of all the synthesized samples are provided in Supporting information 1).

|                  | TiO$_2$ | Fe-TiO$_2$-375 | Fe-TiO$_2$-750 |
|------------------|---------|----------------|----------------|
| Specific BET surface area (m$^2$/g) | 15.1    | 13.8           | 11.8           |

2.2. Photocatalytic Removal of Acetaldehyde

The photocatalytic degradation of gaseous acetaldehyde under visible light irradiation was carried out with TiO$_2$ and Fe-TiO$_2$-300, -375, -450, -525, and -750, and the results are shown in Figure 2. The experiments were carried out with a drop-casted film consisting of pristine TiO$_2$ and the synthesized Fe-TiO$_2$ samples prepared by a drop-casting method (the experimental details can be found in Section 3.3.). Scanning tunneling microscopic (SEM) analysis revealed that each drop-casted film consisted of individual TiO$_2$ particles without noticeable agglomeration among the particles, indicating that the individual TiO$_2$ particles were almost intact after the drop-casting process (Supporting information).

![Figure 2](image-url)  
**Figure 2.** Results of the photocatalysis experiments. Concentration changes of (a) acetaldehyde and (b) CO$_2$ as a function of the visible light irradiation time in the presence of as-received TiO$_2$ (TiO$_2$) and five different Fe-TiO$_2$ samples (Fe-TiO$_2$-300, -375, -450, -525, and -750). (c) Removal efficiencies for acetaldehyde and (d) CO$_2$ selectivity determined after 410 min of visible light irradiation in the presence of TiO$_2$ and Fe-TiO$_2$-300, -375, -450, -525, and -750.
Figure 2a,b show the concentration changes of acetaldehyde and CO$_2$ during the photocatalysis experiments under visible light irradiation. The negative time scales correspond to the pre-adsorption stage in the dark, which was performed prior to the photocatalysis experiments. No notable changes in the concentration of acetaldehyde were observed for any of the TiO$_2$ samples (TiO$_2$ and Fe-TiO$_2$-300, -375, -450, -525, and -750) at the pre-adsorption stage, indicating that the adsorption of acetaldehyde in the dark was negligible for all the cases of the samples.

Upon the visible light irradiation of the surface of all the samples, the concentration of acetaldehyde started to decrease, and that of gaseous CO$_2$ increased without an induction time, showing that the photocatalytic removal of acetaldehyde took place (Figure 2a,b). It is clear that the photocatalytic activity of TiO$_2$ in terms of acetaldehyde removal and CO$_2$ evolution under visible light irradiation was enhanced upon Fe-loading, irrespective of the annealing temperature within the range of 300 to 750 °C (Figure 2a,b). However, the enhancement effects of Fe-loading on the photocatalytic activity of TiO$_2$ under visible light depended on the annealing temperature. Almost all of the gaseous acetaldehyde molecules in the reactor were removed by three Fe-TiO$_2$ samples (Fe-TiO$_2$-300, -375, and -400) after 590 min of blue light irradiation (Figure 2a). By contrast, only roughly half of the acetaldehyde molecules were removed by Fe-TiO$_2$ samples annealed at higher temperatures (Fe-TiO$_2$-525 and -750) under the same experimental conditions (Figure 2a).

One might note that the evolution of CO$_2$ continued even after all the gaseous acetaldehyde molecules in the reactor were removed. For instance, in the presence of Fe-TiO$_2$-375 samples, the concentration of gaseous CO$_2$ continued to increase even after 410 min when the acetaldehyde concentration in the reactor reached zero (Figure 2a,b). This phenomenon can occur when gaseous acetaldehyde is first removed by partial oxidation on the surface of a photocatalyst, and the partially oxidized species is later oxidized into CO$_2$ by a longer exposure to light [28–30]. The formation of acetic acid as an intermediate species on the surface of photocatalysts during the photocatalytic oxidation of acetaldehyde into CO$_2$ was previously reported [28–30]. The previous results indicated that the reaction rate of acetic acid oxidation into CO$_2$ was slower than that of acetic acid formation from acetaldehyde, which can result in the CO$_2$ selectivity being higher than 100% at longer reaction times [28–30].

The concentration change of acetaldehyde during each photocatalysis experiment was further examined by obtaining the C$_{\text{aldehyde measured with each sample at each time}}$/C$_{\text{aldehyde measured without sample}}$ value (%) for acetaldehyde and the acetaldehyde removal efficiency (%) for each duration of light irradiation. The C$_{\text{aldehyde measured with each sample at each time}}$/C$_{\text{aldehyde measured without sample}}$ value (%) for acetaldehyde was calculated as follows in Equation (1):

\[
\frac{\text{Acetaldehyde concentration measured with each sample at each time}}{\text{Acetaldehyde concentration measured without sample}} \times 100 = \frac{C}{C_0} \times 100 \text{ (%) (1)}
\]

The acetaldehyde removal efficiency (%) for each irradiation duration was determined as follows in Equation (2):

\[
\left(1 - \frac{C}{C_0}\right) \times 100 \text{ (2)}
\]

For this calculation, the C$_{\text{aldehyde measured with each sample at each time}}$/C$_{\text{aldehyde measured without sample}}$ of each sample at 410 and 590 min, and the removal efficiency (%) of each sample at 410 min is displayed in Figure 2c. The acetaldehyde removal efficiency of Fe-TiO$_2$ at 410 min increased significantly from that of TiO$_2$ (16.90%) when the Fe-TiO$_2$ sample was annealed at 300 °C (92.88%), and the efficiency was further increased upon the annealing of the Fe-TiO$_2$ sample at 375 °C (100%). On the other hand, as the annealing temperature increased above 375 °C, the enhancement effect of Fe-loading on the photocatalytic activity of TiO$_2$ for acetaldehyde removal under visible light irradiation became less pronounced. In particular, a significant reduction of the enhancement effect of Fe-loading was observed when the annealing temperature was higher than 450 °C. The selectivity of CO$_2$ was calculated for each sample as follows in Equation (3):

\[
\text{The number of gaseous CO}_2\text{ molecules evolved with each sample for each time} \times 2 \times 100 \text{ (3)}
\]
Table 2. Removal efficiencies for acetaldehyde determined after 410 min and 590 min of visible light irradiation in the presence of TiO$_2$ and Fe-TiO$_2$-300, -375, -450, -525, and -750.

|                        | Acetaldehyde removal efficiency at 410 min (%) | Acetaldehyde removal efficiency at 590 min (%) |
|------------------------|-----------------------------------------------|-----------------------------------------------|
| AS-received TiO$_2$    | 16.90                                         | 17.84                                         |
| Fe-TiO$_2$-300         | 92.88                                         | 100                                           |
| Fe-TiO$_2$-375         | 100                                           | 100                                           |
| Fe-TiO$_2$-450         | 87.50                                         | 100                                           |
| Fe-TiO$_2$-525         | 43.31                                         | 56.69                                         |
| Fe-TiO$_2$-750         | 41.35                                         | 56.73                                         |

The denominator corresponds to the number of CO$_2$ molecules generated by the total oxidation of the removed acetaldehyde; the total oxidation of 1 mol of acetaldehyde generates 2 mol of CO$_2$. Figure 2d shows that the CO$_2$ selectivity of the photocatalytic removal of acetaldehyde on the TiO$_2$ surface was also increased by Fe-loading and subsequent annealing. In addition, the enhancement effect of Fe-loading on the CO$_2$ selectivity also depended on the annealing temperature, similarly to the case of the acetaldehyde removal efficiency. The enhancement effects of Fe-loading on the CO$_2$ selectivity were most pronounced when the Fe-TiO$_2$ sample was annealed at 375 $^\circ$C, whereas the effects became significantly less pronounced when the Fe-TiO$_2$ particles were annealed at higher temperatures (525 and 750 $^\circ$C).

2.3. Further Analyses (UV Diffuse Reflectance Spectrophotometry (UV-DRS), Photoluminescence (PL), XPS, and TOF-SIMS)

The Fe-TiO$_2$-375 samples exhibited the highest photocatalytic activity in terms of both acetaldehyde removal and CO$_2$ evolution under visible light irradiation among the five Fe-TiO$_2$ samples (Fe-TiO$_2$-300, -375, -450, -525, and -750). The enhancement effects of Fe-loading on the photocatalytic activity of TiO$_2$ were reduced with increasing annealing temperature, and in particular, annealing at temperatures higher than 450 $^\circ$C led to a significant reduction of the photocatalytic activity of Fe-TiO$_2$. In order to understand the annealing temperature dependency of the enhancement effects of Fe-loading, three representative samples (Fe-TiO$_2$-375, -525, and -750) were further analyzed by UV-DRS, PL, XPS, and TOF-SIMS.

The UV-vis reflectance of each sample was measured, and the obtained reflectance values were converted into values corresponding to the absorption values based on the Kubelka–Munk function [31–33] (Figure 3a). The UV-vis reflectance of the TiO$_2$ samples was also measured, and the values obtained using the Kubelka–Munk function are displayed in Figure 3a for comparison. The optical band gap of each sample can be determined by obtaining the X-axis intercept values of the extrapolated straight line of each Kubelka–Munk plot, and the optical band gap of TiO$_2$ was determined to be ~3.01 eV. The optical band gap of TiO$_2$ was reduced upon the Fe-loading and subsequent annealing (Figure 3a), and higher temperature annealing at 750 $^\circ$C reduced the optical band gap a little further than in the cases of annealing at 375 and 525 $^\circ$C. However, the modification effects on the optical band gap of TiO$_2$ did not seem to be significant; the band gap value of the Fe-TiO$_2$-750 sample was determined to be ~2.96 eV. In addition, the optical band gap changes upon Fe-loading, and the annealing did not correlate to the annealing temperature dependency of the modification effects on the photocatalytic activity of the Fe-TiO$_2$ samples; Fe-TiO$_2$-375 exhibited significantly higher photocatalytic activity than Fe-TiO$_2$-525 and -750, but the band gap reduction was most pronounced for the case of the Fe-TiO$_2$-750 sample. We would also like to mention that the optical band gaps of other synthesized Fe-TiO$_2$ samples (Fe-TiO$_2$-300, -450, and -525) were also determined, and the variation among all the synthesized samples and pristine TiO$_2$ were only marginal (Supporting information). These results indicate that the modification effects on the photocatalytic activity and its annealing temperature dependency cannot be simply explained by the optical band gap reduction due to Fe-loading and thermal annealing.
An Al 2p core-level XPS peak centered at ~75 eV was also observed for all three samples (Figure 4b), whereas increased annealing temperatures (>375 °C, e.g., 525 and 750 °C) resulted in the reduction of the enhancement of the charge separation efficiency by Fe-loading.

Later, three Fe-TiO2 samples (Fe-TiO2-375, -525, and -750) were analyzed by two surface sensitive analysis techniques (XPS and TOF-SIMS), and the results are shown in Figures 4 and 5. Figure 4a–c show the Ti 2p, Fe 2p, and Al 2p core-level XPS spectra, respectively, of the three Fe-TiO2 samples. The intensity of each XPS spectrum was normalized to the respective Ti 2p peak intensity. The binding energy of the Ti 2p_{3/2} peaks of all three samples were ~ 458.7 eV, corresponding to Ti^{4+} states [34–36], and the peak shapes and positions for the three samples were almost identical to each other (Figure 4a). An Al 2p core-level XPS peak centered at ~75 eV was also observed for all three samples (Figure 4b)
attributed to the existence of the alumina shell on the as-received TiO₂ particles. Note that alumina shells are generally considered to be required to increase the compatibility of TiO₂ with plastics or binders forming more uniform composite functional structures. In Supporting information, the Ti 2p and Al 2p core-level XPS spectra of the as-received TiO₂ are displayed together with those of the three Fe-TiO₂ samples (Fe-TiO₂-375, -525, and -750). It is shown that the Ti 2p and Al 2p XPS spectra did not undergo significant changes upon the modification, excepting for the slight decrease in the Al 2p signal with the increase in the annealing temperature after Fe deposition from 375 to 750 °C (Supporting information). It is also worth noting that a significant Ti signal was detected together with the Al signal in the XPS analysis, although the surface of as-received TiO₂ was covered with alumina, indicating that either the alumina shell was very thin (~ 2 nm) or the surface of the TiO₂ was not completely covered by the alumina shell.

Figure 4. Results of XPS analysis. (a) Ti 2p, (b) Al 2p, and (c) Fe 2p core-level XPS spectra of Fe-TiO₂-375, -525, and -750 samples.
All the measured secondary ion signals are summarized in Supporting information. The secondary signals of three samples divided by the respective Ti + signal. (b) $\text{FeTi}^+$ signals of each sample were divided by the respective FeO + signals are compared.

Upon Fe-loading and annealing, Fe 2p$_{3/2}$ core-level XPS peaks appeared in the binding energy region of 713–703 eV (Figure 4c). The intensities of the Fe 2p core-level XPS spectra of the Fe-TiO$_2$ samples decreased with increasing annealing temperature, especially when the temperature was increased from 375 to 525 °C. This is similar to the case of the Al 2p core-level XPS spectra, where an intensity decrease was observed upon annealing at higher temperature, but the decrease in Fe 2p signal was more pronounced than that in the case of the Al 2p core-level. Along with the decrease in the Fe 2p signal intensity, a shift of the Fe 2p XPS peaks to the lower binding energy region was observed upon the higher temperature annealing; the Fe 2p$_{3/2}$ peak of Fe$\text{-TiO}_2$-375 was centered at ~710 eV, whereas the center position of the Fe 2p$_{3/2}$ peak of Fe$\text{-TiO}_2$-525 was at ~707 eV. The Fe 2p$_{3/2}$ peak position of Fe$\text{-TiO}_2$-375 corresponded to oxidic Fe either in Fe(II) or Fe(III); by contrast, the peak positions of the two Fe-TiO$_2$ samples annealed at higher temperatures (Fe-TiO$_2$-525 and -750) corresponded to Fe atoms in the metallic state or Fe(I) state. Both the intensity decreases and the lower binding energy shift of the Fe 2p XPS peak with increasing annealing temperatures (>375 °C) seemed to be caused by the strong metal–support interaction (SMSI) of TiO$_2$ with the loaded Fe-oxide. The SMSI between the group VIII metals (e.g., Fe and Ni) and TiO$_2$ substrate had been reported, which varied the catalytic activities of the metals (metal oxides) of the group VIII atoms regarding Fischer–Tropsch (F-T) synthesis [37–39]. The SMSI between Fe-oxide and TiO$_2$ can result in (1) the encapsulation of the Fe-oxide by the TiO$_2$ (the scrambling up of the underlying TiO$_2$ [40–42] or interdiffusion of the Fe atoms into the TiO$_2$ substrate [43–46]) and (2) the reduction of the Fe-oxide by the charge transfer [43–46]. The surface structure changes of the Fe$\text{-TiO}_2$ samples upon higher temperature annealing due to SMSI effects were further evidenced by the TOF-SIMS analysis, the details of which are discussed below.

Three Fe-TiO$_2$ samples (Fe$\text{-TiO}_2$-375, -525, and -750) were further analyzed by TOF-SIMS using a B$_3$ + ion beam as a primary ion source. The intensities of the secondary ion signals measured by TOF-SIMS for each type of sample were normalized to the respective signal intensity of the Ti + ion. All the measured secondary ion signals are summarized in Supporting information. The secondary mass signals other than Al$^+$ and Fe$^+$ were categorized into two groups, Fe$_x$O$_y$ + and Fe$_x$Ti$_y$ +, as shown in Figure 5a. The intensity of Fe$\text{O}_y$+ corresponds to the sum of the secondary ion signals containing Fe and O atoms, e.g., FeO$^+$, FeO$_2$, Fe$_2$O$^+$, etc., whereas the Fe$_x$Ti$_y$ + intensity shown in Figure 5a corresponds to the sum of the secondary ion signals containing Fe and Ti atoms. As the annealing temperature for the Fe-TiO$_2$ increased above 375 °C, the intensities of Fe$_x$O$_y$ + and Fe$_x$Ti$_y$ + with respect to Ti + gradually decreased, indicating the pronounced diffusion of Ti atoms to the top surface of the Fe-TiO$_2$ sample at higher temperatures (525 and 750 °C), which resulted in the higher coverage of the...
When these processes take place, the electron-hole separation efficiency of the loaded Fe-oxide surface by TiO$_2$. It is important to note that the decrease in the Fe$_x$O$_{y+x}$$^+$/Ti$^+$ signal with increasing annealing temperatures above 375 °C was more pronounced than in the Fe$_x$Ti$_y$$^/Ti^+$ case. Figure 5b compares the Fe$_x$Ti$_y$$^/signal to FeO$_{y+x}$$^+$ signal ratios of three samples (Fe-TiO$_2$-375, -525, and -750). An increase in the Fe$_x$Ti$_y$$^+/FeO$_{y+x}$$^+$ signal ratio was notable as the annealing temperature was increased above 375 °C. The SIMS data only monitor the topmost surface structure, and therefore, intermixing between Fe and Ti in deeper layers is not fully reflected here. Nevertheless, these results indicate that the interaction between Fe and TiO$_2$ became stronger at higher temperatures (especially >375 °C), which can lead to more interdiffusion of Ti atoms to the loaded Fe-oxide and the reduction of the loaded Fe-oxide by TiO$_2$ (forming a compound such as FeTi$_2$O$_{3-x}$, in which Fe has an oxidation state of II or I). The SIMS analysis results were in line with the results of XPS analysis; both analysis results indicated the stronger SMSI effects of TiO$_2$ on the loaded Fe-oxide upon Fe-TiO$_2$ annealing at higher temperature (>375 °C). It is worth noting that both the SIMS and XPS analysis methods are surface-sensitive techniques, of which the typical analysis depths are ~2 nm and ~5 nm from the topmost surface, respectively.

We suggested the following scenario, which can reconcile all our observations of UV/vis, PL, XPS, SIMS, and the temperature dependency of the enhancement effects of Fe-loading on the photocatalytic activity of Fe-TiO$_2$ samples (Figure 6a). The electron-hole pairs were generated upon photon absorption. Electrons in the conduction band (or holes in the valence band) can transfer into Fe(II) atoms, reducing Fe(II) atoms into Fe(II) states (or oxidizing Fe(III) atoms into Fe(IV) states). If the Fe atoms in Fe(II) states (or Fe(IV) states) were available to the oxygen molecules (or water) adsorbed on the surface, electrons (or holes) could further transfer into oxygen molecules (or water), generating O$_2^-$ ions (or OH radicals), and then the Fe atoms would return to the original Fe(III) states (Figure 6a). When these processes take place, the electron-hole separation efficiency of the Fe-TiO$_2$ samples under light irradiation can be improved, which can lead to the increased photocatalytic activity of Fe-TiO$_2$. 

![Figure 6. Cont.](image-url)
The Fe-P25-750 sample exhibited slightly better photocatalytic performance in terms of acetaldehyde removal and CO$_2$ evolution compared to the Fe-TiO$_2$-375 sample. The modification process for the Fe-TiO$_2$-375 consumed much less energy than that for Fe-P25-750, owing to the lower temperature of the thermal annealing process (375 $^\circ$C) compared to 750 $^\circ$C for the P25 sample. The Fe-P25-750 sample containing 0.1 wt% of Fe was prepared via the tr-CVD of Fe-oxide and thermal annealing [28]. The photocatalytic removal of acetaldehyde on the surface of Fe-P25-750 was performed under the same conditions as in the Fe-TiO$_2$-375 case (Figure 7a,b). The Fe-P25-750 sample exhibited slightly better photocatalytic performance in terms of acetaldehyde removal and CO$_2$ evolution compared to the Fe-TiO$_2$-375 sample under the same conditions; a 100% removal efficiency was achieved on the surface of Fe-TiO$_2$-375 by 410 min of visible light irradiation. However, one should note that the TiO$_2$ used as a base material for Fe-TiO$_2$-375 in this work was produced via a sulfuric acid method, and its price (3 USD/g) is much lower than that of the P25 (50–70 USD/g). In addition, the modification process for the Fe-TiO$_2$-375 sample seemed to be a more favorable choice for industrial applications than Fe-P25-750.

2.4. Large-Scale Production of Catalysts and Their Potential Applications

Finally, we explored the potential applications of the Fe-TiO$_2$-375 particles. Firstly, we compared the photocatalytic activity of the Fe-TiO$_2$-375 sample with that of the Fe-loaded (0.1 wt% of Fe) commercial TiO$_2$ particles (P25, Evonik) annealed at 750 $^\circ$C, hereafter denoted as Fe-P25-750. Previously, the Fe-P25-750 sample has been proven to exhibit the highest photocatalytic activity regarding acetaldehyde degradation under visible light irradiation among the P25 samples modified by the tr-CVD of Fe-oxide and thermal annealing [28]. The Fe-P25-750 sample containing 0.1 wt% of Fe was prepared via the tr-CVD of Fe-oxide on commercially available TiO$_2$ (P25, Evonik) and subsequent annealing at 750 $^\circ$C, as described in the literature [28]. The photocatalytic removal of acetaldehyde on the surface of Fe-P25-750 was performed under the same conditions as in the Fe-TiO$_2$-375 case (Figure 7a,b). The Fe-P25-750 sample exhibited slightly better photocatalytic performance in terms of acetaldehyde removal and CO$_2$ evolution compared to the Fe-TiO$_2$-375 sample under the same conditions; a 100% removal efficiency for acetaldehyde was achieved by 370 min of visible light irradiation on the surface of Fe-P25-750, whereas a 100% removal efficiency was achieved on the surface of Fe-TiO$_2$-375 by 410 min of visible light irradiation. However, one should note that the TiO$_2$ used as a base material for Fe-TiO$_2$-375 in this work was produced via a sulfuric acid method, and its price (3 USD/g) is much lower than that of the P25 (50–70 USD/g). In addition, the modification process for the Fe-TiO$_2$-375 sample seemed to be a more favorable choice for industrial applications than Fe-P25-750.
One of the potential applications of photocatalyst particles for improving outdoor or indoor air quality is putting those particles on the outside or inside walls of buildings. In order to explore this possibility, samples of Fe-TiO $\text{}_2$-375 particles were mixed with a commercially available paint and a surface hardening agent, and the mixtures were spread on a stainless steel (SUS) plate and a cement block, respectively. Then, the photocatalytic removal of acetaldehyde under visible light in the presence of Fe-TiO $\text{}_2$-375 particles (8 kg) produced in one sequential tr-CVD and annealing process was 40 times greater than that in the aforementioned case (200 g). The photocatalytic activity of the mass-produced Fe-TiO $\text{}_2$-375 regarding acetaldehyde removal under the visible light irradiation was examined under the same conditions as for the case of the Fe-TiO $\text{}_2$-375 produced at a small scale (200 g per sequential tr-CVD and annealing process) (Figure 7c,d). The mass-produced Fe-TiO $\text{}_2$-375 exhibited a slightly lower efficiency of acetaldehyde removal (100% acetaldehyde removal at 600 min) than the Fe-TiO $\text{}_2$-375 sample produced at the small scale, which was most likely due to the existence of an induction period for the activity of the mass-produced samples due to the higher level of impurities, but it exhibited slightly higher efficiency in terms of CO$_2$ evolution. The results demonstrated the feasibility of the mass production of Fe-TiO $\text{}_2$-375 and its usability as a photocatalyst for air purification.

We also tested the possibility of the mass production of Fe-TiO $\text{}_2$-375 photocatalysts. The Fe-TiO $\text{}_2$-375 samples were produced on a much larger scale; the amount of Fe-TiO $\text{}_2$-375 particles (8 kg) produced in one sequential tr-CVD and annealing process was 40 times greater than that in the aforementioned case (200 g). The photocatalytic activity of the mass-produced Fe-TiO $\text{}_2$-375 regarding acetaldehyde removal under the visible light irradiation was examined under the same conditions as for the case of the Fe-TiO $\text{}_2$-375 sample produced at small scale and mass-produced Fe-TiO $\text{}_2$-375.

Figure 7. The results of the photocatalysis experiments (Fe-P25-750 and mass-produced Fe-TiO $\text{}_2$-375). Concentration changes of (a) acetaldehyde and (b) CO$_2$ as a function of the visible light irradiation (Table 2) and Fe-P25-750 samples. Concentration changes of (c) acetaldehyde and (d) CO$_2$ as a function of the visible light irradiation time in the presence of Fe-TiO $\text{}_2$-375 produced at small scale and mass-produced Fe-TiO $\text{}_2$-375.

Concentration changes of (a) acetaldehyde and (b) CO$_2$ as a function of the visible light irradiation time in the presence of Fe-TiO $\text{}_2$-375 samples. Concentration changes of (c) acetaldehyde and (d) CO$_2$ as a function of the visible light irradiation time in the presence of Fe-TiO $\text{}_2$-375 produced at small scale and mass-produced Fe-TiO $\text{}_2$-375.

We also tested the possibility of the mass production of Fe-TiO $\text{}_2$-375 photocatalysts. The Fe-TiO $\text{}_2$-375 samples were produced on a much larger scale; the amount of Fe-TiO $\text{}_2$-375 particles (8 kg) produced in one sequential tr-CVD and annealing process was 40 times greater than that in the aforementioned case (200 g). The photocatalytic activity of the mass-produced Fe-TiO $\text{}_2$-375 regarding acetaldehyde removal under the visible light irradiation was examined under the same conditions as for the case of the Fe-TiO $\text{}_2$-375 produced at small scale (200 g per sequential tr-CVD and annealing process) (Figure 7c,d). The mass-produced Fe-TiO $\text{}_2$-375 exhibited a slightly lower efficiency of acetaldehyde removal (100% acetaldehyde removal at 600 min) than the Fe-TiO $\text{}_2$-375 sample produced at the small scale, which was most likely due to the existence of an induction period for the activity of the mass-produced samples due to the higher level of impurities, but it exhibited slightly higher efficiency in terms of CO$_2$ evolution. The results demonstrated the feasibility of the mass production of Fe-TiO $\text{}_2$-375 and its usability as a photocatalyst for air purification.

One of the potential applications of photocatalyst particles for improving outdoor or indoor air quality is putting those particles on the outside or inside walls of buildings. In order to explore this possibility, samples of Fe-TiO $\text{}_2$-375 particles were mixed with a commercially available paint and a surface hardening agent, and the mixtures were spread on a stainless steel (SUS) plate and a cement block, respectively. Then, the photocatalytic removal of acetaldehyde under visible light in the presence
of each sample was examined under the same experimental conditions as in the aforementioned case (Fe-TiO$_2$-375 drop-casted on a SUS plate) (Figure 8a,b). For both cases, the initiation of the photocatalytic removal of acetaldehyde and CO$_2$ evolution was observed upon visible light irradiation (Figure 8a,b). It is interesting that both samples exhibited similar acetaldehyde removal efficiency, but the Fe-TiO$_2$-375 on the cement block showed a much higher efficiency of CO$_2$ evolution than the Fe-TiO$_2$ on the paint. This might be caused by the different natures of the adhesive materials between the two samples, but further systematic investigations are needed to reveal the effects of the adhesive materials on the photocatalytic activity of TiO$_2$-based particles. Nevertheless, it is worth noting that the Fe-TiO$_2$-375 particles can exhibit their photocatalytic activity under visible light irradiation after being mixed with other adhesive materials, which makes them applicable for air purification in outdoor or indoor environments.

![Figure 8. The results of the photocatalysis experiments (Fe-TiO$_2$-375 mixed with paint or adhesive materials). Concentration changes of (a) acetaldehyde and (b) CO$_2$ as a function of the visible light irradiation time in the presence of Fe-TiO$_2$-375 mixed with paint or a surface hardening agent and spread on a stainless steel surface or on a cement block, respectively.](image)

3. Materials and Methods

3.1. Preparation of Photocatalysts

3.1.1. Small-Scale Production

FeO$_x$/TiO$_2$ photocatalysts were prepared by a temperature-regulated chemical vapor deposition (tr-CVD) method. Commercial titanium dioxide (TiO$_2$), bought from Lomo Billions, China, was used as a substrate. Bis(cyclopentadienyl)iron (Ferrocene, Fe(Cp)$_2$, Sigma Aldrich, USA) was used as a metal precursor, whereas oxygen and water in ambient air were used as the oxidizing agent. Two hundred grams of TiO$_2$ was mixed with 0.667 g of Fe(Cp)$_2$ (weight ratio of 300:1), and the mixture was placed in a quartz beaker (250 mL). Our previous studies showed that Fe-loading of less than 2% can have a significant enhancement effect on photocatalytic activity [28]. We used a different Fe-loading here, and the Fe-loading of 0.4 wt% prepared by a 1:300 ratio of TiO$_2$ and Fe(Cp)$_2$ resulted in better CO$_2$ selectivity, even though the acetaldehyde removal rate appeared to be less sensitive to the Fe-loading in this range (Supporting information). Thus, we concentrated on the Fe-loading of 0.4 wt% in the present work. The top part of the quartz beaker was covered with aluminum foil, and the gap between the beaker and aluminum foil was sealed with polyimide (PI) tape. The beaker was located in a box furnace (DMF-3T, UITECH, Hwaseong, Korea) with an internal volume of 3 L. The temperature was increased to 60 °C and kept at 60 °C for 1 h for the evaporation of the Fe(CP)$_2$. After 1 h, the temperature was increased to 200 °C, and this temperature was maintained for 1 h to oxidize the Fe(CP)$_2$ on the surface of TiO$_2$. The aluminum foil and PI tape were removed after the beaker was cooled down to room temperature. After the evaporation of Fe(CP)$_2$, the top part of the quartz beaker was covered with aluminum foil, and the gap between the beaker and aluminum foil was sealed with polyimide (PI) tape. The beaker was located in a box furnace (DMF-3T, UITECH, Hwaseong, Korea) with an internal volume of 3 L. The temperature was increased to 200 °C, and this temperature was maintained for 1 h to oxidize the Fe(CP)$_2$ on the surface of TiO$_2$. The temperature was further increased to 200 °C, and this temperature was maintained for 1 h to oxidize the Fe(CP)$_2$ on the surface of TiO$_2$. The aluminum foil and PI tape were removed after the beaker was cooled down to room temperature.
temperature. Then, the tr-CVD-prepared samples were further annealed at various temperatures (300, 375, 450, 525, and 750 °C) for 2 h under ambient conditions. Hereafter, the Fe-oxide-loaded TiO\textsubscript{2} samples prepared via the tr-CVD of Fe-compounds and subsequent annealing at various temperatures are referred as Fe-TiO\textsubscript{2}-annealing temperature, e.g., Fe-TiO\textsubscript{2}-375 for 375 °C-annealed Fe-deposited TiO\textsubscript{2} sample, whereas TiO\textsubscript{2} is referred to as the as-received TiO\textsubscript{2}.

3.1.2. Large-Scale Production

For the mass production of the Fe-deposited TiO\textsubscript{2} photocatalysts, a box furnace (PMF27, LAB HOUSE, Seoul, Korea) with a larger internal volume (27 L) was used, and the quartz beaker was replaced by an alumina crucible (size, 135 mm × 135 mm × 60 mm). Eight kilograms of TiO\textsubscript{2} was mixed with 27 g of Fe(Cp)\textsubscript{2} for 30 min using a cement mixer (DCM-300R, DCM corporation, Yangsan, Korea). The mixture of TiO\textsubscript{2} and Fe(Cp)\textsubscript{2} was distributed in the alumina crucibles (15 EA). The top of each alumina crucible was covered with an alumina lid, and the gap between the crucible and the lid was sealed with PI tape. Then, the crucibles were placed in the box furnace (internal volume of 27 L), and the tr-CVD of Fe-oxide on TiO\textsubscript{2} particles was initiated by increasing the temperature in the same manner as in the aforementioned case (small-scale production, 1 h of 60 °C-heating followed by 1 h of 200 °C-heating). After the tr-CVD of the Fe-compound on the TiO\textsubscript{2} particles, the crucibles were cooled down until the temperature reached room temperature, and then the lids and PI tape were removed from the tops of all the crucibles. Then, the Fe-TiO\textsubscript{2} was further annealed at 375 °C for 2 h under ambient conditions using the same furnace (27 L-box furnace).

3.2. Characterization of Photocatalysts

The amounts of the Fe loading of Fe-TiO\textsubscript{2} were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian, Agilent, Santa Clara, California, USA). Three samples (TiO\textsubscript{2}, and Fe-TiO\textsubscript{2}-375 and -750) were selected for transmission electronic microscopy (TEM), X-ray diffraction (XRD), and surface area analyses. Structural images of three samples were obtained using TEM (JEM-3010, Jeol, Japan). The crystallinity of each sample was studied by obtaining X-ray diffraction (XRD) patterns using a diffractometer (Ultima IV, Rigaku, Tokyo, Japan) and Cu Ka radiation. The N\textsubscript{2} adsorption/desorption isotherm (3Flex, Micromeritics, Norcross, Georgia, USA) of each sample was obtained, and the surface area of each sample was determined using the Brunauer–Emmett–Teller (BET) method.

TiO\textsubscript{2} and Fe-TiO\textsubscript{2}-375, Fe-TiO\textsubscript{2}-525, and Fe-TiO\textsubscript{2}-750 samples were characterized with a UV-Vis diffuse reflectance spectrophotometer (UV-DRS, UV-3600, SHIMADZU, Japan) and photoluminescence spectrometer (FS-2, SCINCO, Seoul, Korea). The surfaces of four samples (TiO\textsubscript{2}, and Fe-TiO\textsubscript{2}-375, -525, and -750) were also analyzed by X-ray photoelectron spectroscopy (XPS). XPS measurements were carried out under ultra-high vacuum conditions with a base pressure of 5.0 × 10\textsuperscript{-10} Torr. The XPS spectrum of each sample was collected by a concentric hemispherical analyzer (CHA, PHOIBOS-HSA3500, SPECS, Berlin, Germany) in a fixed pass energy mode (30 eV), and Mg Ka radiation (1253.6 eV) was used.

Time-of-flight SIMS (TOF-SIMS) analyses were performed for the three selected Fe-TiO\textsubscript{2} samples (Fe-TiO\textsubscript{2}-375, -525, and -750) using a TOF-SIMS 5 (ION-TOF GmbH, Muenster, Germany). The instrument was equipped with a Bi liquid metal ion gun aligned along the axes at 45° to the surface of the sample. For SIMS analysis, Bi\textsubscript{3+} was used as the primary ion with an acceleration voltage of 30 keV, and the secondary positive ions emitted from the surface of the sample were analyzed with the TOF mass spectrometer. The pressed pellet of each sample was mounted on the sample stage of the chamber using carbon tape. A 500 µm × 500 µm area of the sample was analyzed, and each SIMS spectrum was obtained by accumulating signals from 30 scans. The mass scale of the SIMS experiment was calibrated using H\textsuperscript{+}, CH\textsubscript{3}\textsuperscript{+}, C\textsubscript{2}H\textsubscript{5}\textsuperscript{+}, C\textsubscript{3}H\textsubscript{7}\textsuperscript{+}, and C\textsubscript{4}H\textsubscript{9}\textsuperscript{+}. 
3.3. Photocatalytic Decomposition of Acetaldehyde

The photocatalytic removal of acetaldehyde on the surface of TiO$_2$ samples (TiO$_2$ and Fe-TiO$_2$-300, -375, -450, -525, and -750) was studied under visible light irradiation using a batch-type reactor (Supporting information). A high vacuum chamber (base pressure of $\sim 2.0 \times 10^{-5}$ Torr, reactor volume of $\sim 5.3$ L) was used as a reactor, and it was equipped with a convection vacuum gauge (SUPER BEE, InstruTech, Longmont, Colorado, USA), oil rotary (W2V40, WSA CO. LTD., Hwaseong, Korea), and turbomolecular pump (TMG 260P, PFEIFFER VACUUM Technology AG, Germany). The chamber was connected to the gas chromatograph (GC, HP 6890 series, Hewlett Packard) via $\frac{1}{4}$" SUS lines equipped with an HP-PLOT/Q column (1909/SP-Q04, 30 m $\times$ 0.530 mm $\times$ 40 $\mu$m, Agilent, Santa Clara, California, USA) and flame ionization detector (FID). Along the $\frac{1}{4}$" SUS lines, a diaphragm pump (DA70EEAC, flow rate of 7 L/min, YLKTECH) was installed between the GC and chamber to circulate the gas through the reactor. Polytetrafluoroethylene (PTFE) tubes ($\frac{1}{4}$") were used for the inlet and outlet lines of the diaphragm pump to accommodate the vibration of the diaphragm pump. The top side of the chamber was composed of a quartz view port, which allowed the efficient transmission of light from the light source located on the outside of the chamber.

The thin film of each photocatalyst was prepared by drop-casting 0.15 g of each sample on a SUS (stainless steel) plate ($6 \times 6$ cm$^2$) [28], and it was mounted on the sample stage of the chamber. After the sample mounting, the reactor was pumped down until the reactor pressure reached $\sim 2.0 \times 10^{-5}$ Torr, and then the reactor was filled with a gas mixture (total pressure of 760 Torr) consisting of H$_2$O, O$_2$, dry air, and acetaldehyde diluted with N$_2$ (201 mol ppm). Each gas was injected into the reactor using a leak valve while monitoring its partial pressure with the vacuum gauge. The composition of the total gas mixture corresponded to ambient air containing 30 ppm of acetaldehyde with a relative humidity (RH) of 33% at 25 °C. After the reactor was filled with the gas mixture, the diaphragm pump was turned on to circulate the gas mixture through the reactor. Every 10 min, 50 $\mu$L of the gas mixture inside the reactor was injected into the GC to monitor the acetaldehyde and CO$_2$ concentration. Prior to the initiation of the GC analysis, the gas mixture in the reactor was pre-circulated by the diaphragm pump for 30 min in the dark to achieve a homogeneous gas composition throughout the reactor. The adsorption of acetaldehyde on each sample was monitored for 3 h in the dark. The blue LED lamp emitted visible light with a maximum intensity at 460 nm. The wavelength of the emitted light was in the range of 420–490 nm (Supporting information), and the distance between the blue LED and sample surface was 10 cm. The reactor temperature was kept at $\sim 24$ °C throughout the experiments by controlling the temperature of the laboratory using an air conditioning system. The standard deviation of the reactor temperature over 10 h was 0.32 °C (24.3 °C ± 0.32 °C). We would like to mention that our testing method for the photocatalytic removal of acetaldehyde is different from the ISO standard method (ISO 22197-2:2011, details are provided in Supporting information). The main difference between our method and the ISO standard is that a batch-type reactor was used in this study, which is beneficial for examining the reaction rates compared to the flow-type reactor (ISO standard).

Additional photocatalytic experiments were performed with a selected Fe-TiO$_2$ sample (Fe-TiO$_2$-375) to demonstrate the potential applications of the Fe-loaded TiO$_2$ sample. For this purpose, samples of Fe-TiO$_2$-375 were mixed with a surface hardening agent (BUFFHARD, STEL corporation, Korea) and a paint (NOROO, Korea), and the resulting mixtures were loaded on a cement block ($6 \times 6$ cm$^2$) and SUS plate ($6 \times 6$ cm$^2$), respectively. The Fe-TiO$_2$-375 content in each mixture (Fe-TiO$_2$-375 mixed with surface hardening agents and Fe-TiO$_2$-375 mixed with paint) was 10 wt%, and 1 g of each mixture was loaded. The photocatalytic experiment with these samples was carried out in the same manner, and under the same conditions, as those performed with the TiO$_2$ thin films on SUS plates.

4. Conclusions

Commercial rutile TiO$_2$ particles (200–300 nm) whose surfaces were covered with a thin alumina shell were modified by the tr-CVD of Fe-oxide (0.4 wt%) and subsequent thermal annealing in the temperature range of 300–750 °C. The particle size and crystallinity of the rutile TiO$_2$ particles
were not changed by the modification. The photocatalytic performance of the TiO$_2$ in terms of acetaldehyde removal and CO$_2$ evolution under visible light irradiation was significantly enhanced by the modification. The enhancement effect of the Fe-loading was dependent on the annealing temperature (300–750 °C), and the effect was most pronounced at 375 °C. The enhancement effect decreased gradually as the annealing temperature increased above 375 °C, and in particular, the Fe-TiO$_2$-525 and Fe-TiO$_2$-750 samples showed significantly lower activity than the Fe-TiO$_2$-375 sample.

Three representative Fe-TiO$_2$ samples (Fe-TiO$_2$-375, -525, and -750) were further analyzed using various techniques, including two surface-sensitive methods (XPS and TOF-SIMS). The higher-temperature annealing (525 and 750 °C) led to the stronger metal support interactions of TiO$_2$ with the structure of oxidized Fe. It resulted in the reduction of the oxidation states of the loaded Fe-oxide as well as a decrease in the surface Fe-oxide available to the adsorbed molecules at the higher annealing temperature (>375 °C). These effects resulted in the decreased charge separation efficiency of the Fe-TiO$_2$ sample under light irradiation, which led to the reduction of the enhancement effect of Fe-loading on the photocatalytic activity of the Fe-TiO$_2$ sample.

Furthermore, we demonstrated that the amounts of Fe-TiO$_2$-375 sample produced in one sequential tr-CVD and annealing process can be easily increased up to 8 kg from 200 g. The mass-produced sample also exhibited photocatalytic activity regarding acetaldehyde removal under visible light that was comparable to that of the small-scale-produced Fe-TiO$_2$-375 sample. In addition, the Fe-TiO$_2$-375 particles exhibited noticeable photocatalytic activity regarding acetaldehyde removal under visible light after they were mixed with either paint or a surface-hardening agent and spread on the SUS or on a cement block. These results showed the high applicability of the Fe-modified rutile TiO$_2$ for applications for air purification in either outdoor or indoor environments.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/7/739/s1.

- Figure S1: (a) Ti 2p and (b) Al 2p core-level XPS spectra of TiO$_2$ and Fe-TiO$_2$-375, -525, and -750 samples.
- Figure S2: Summary of all measured secondary ion signals.
- Figure S3: Concentration changes of (a) acetaldehyde and (b) CO$_2$ as a function of the visible light irradiation time in the presence of two different Fe-TiO$_2$ samples (0.4 wt% Fe-TiO$_2$-375 and 1.6 wt% Fe-TiO$_2$-375).
- Figure S4: Experimental set up of the batch type reactor for the measurement of photocatalytic activity.
- Figure S5: Intensity of blue light measured by using a luminance spectrophotometer (CL-500A, Konica Minolta, Japan).

Author Contributions: S.Y.K., data curation, formal analysis, investigation, and methodology; S.S., data curation and methodology; B.I.C., formal analysis and methodology; S.Z., formal analysis and investigation; H.O.S., data curation, validation, writing—original draft, and writing—review and editing; Y.D.K., conceptualization, funding acquisition, project administration, resources, and writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2018R1D1A1B07040916) (2017R1D1A1B03034381) and a research grant from the Korea Basic Science Institute (D010100).

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

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