

Article

Enhancement of Visible-Light Photocatalytic Efficiency of TiO₂ Nanopowder by Anatase/Rutile Dual Phase Formation

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Abstract: Visible-light photocatalytically active titanium oxide (TiO₂) nano-powder was synthesized by a flat-flame chemical vapor condensation method. The formation of TiO₂ consisting of different ratios of anatase and rutile phases was controlled by two parameters: the acetylene flow rate (C₂H₂, 600 sccm and 800 sccm) and the acetylene/oxygen flow ratio (C₂H₂/O₂, 1:3, 1:4, 1:5, and 1:6). The location of the photonic center was identified for visible-light absorption, which is in the anatase grains. The photonic center on the surface of anatase grains happens to be the nucleation site for rutile in an oxygen-deficient environment. The visible-light absorption could be attributed to the formation of defect levels related to the photonic center within the band gap of anatase. The major role of the mixed-phase structure of TiO₂ in the enhancement of visible-light photocatalytic activity is in the enhancement of carrier separation and not of light harvest, for the powder produced in this study.

Keywords: titanium oxide; anatase; rutile; nucleation; photonic center; photocatalyst; dual phases; phase transformation; visible light; nanopowder

1. Introduction

Titanium dioxide has long been considered an excellent photocatalyst in many aspects. It has many advantages, such as insolubility in acid and alkali, nonoccurrence of light corrosion under sunlight, chemical stability, non-toxicity for humans, and the abundance of its elements in the Earth's crust [1]. When TiO₂ absorbs photons from the light, it generates electron-hole pairs [2–4]. Subsequently, electrons and holes react with oxygen and water which adsorb on the surface of TiO₂ to form the active oxygen species, such as OH radicals and O₂^{•−} ions, for the catalytic reaction. TiO₂ exists mainly in four phases, which are anatase, rutile, brookite, and TiO₂(B) [5,6]. Anatase is thought to be the best photocatalyst, among others [7,8]. Unfortunately, pure anatase is inhibited for use under visible light by its wide bandgap of 3.2 eV, since it can only absorb the bandgap equivalent UV light for electron excitation. Only about 4% of the energy in the solar spectrum belongs to UV light, while 45% of the energy belongs to visible light. Having this in mind, many scientists have tried to improve the photocatalytic activity by expanding the absorption spectrum into the visible light region either by doping [9–11] or by alloying to enhance light harvesting, and this approach has achieved various degrees of success. Another strategy for photocatalytic efficiency improvement is to form mixed-phase TiO₂. Many studies have shown that mixed anatase and rutile TiO₂ powders exhibit better photocatalytic activity than does either pure phase [12–15]. An investigation revealed that the conduction band edge of rutile is 0.2 eV lower than that of anatase [16]. When the electrons are excited from the valence band in the mixed phase by UV light, some of the electrons in the conduction

band of anatase may transfer to the conduction band of rutile and suppress the recombination of electron-hole pairs [17,18]. There are studies in the literature reporting phase transformation of TiO_2 , which may help us in preparing anatase/rutile dual phases [19–22]. In this work, we synthesized mixed-phase TiO_2 photocatalyst by using a flat-flame chemical vapor condensation (FFCVC) method, and the mixed phases and location of the photonic center for visible-light absorption were examined. Also, we determined the trends of methylene blue degradation of samples with different ratios of anatase and rutile. We also confirm that the nanopowder we produced not only absorbs visible light, but also possesses photocatalytic activity, and we conclude the role of the anatase/rutile interface on the enhancement of photocatalytic activity under visible light illumination.

2. Materials and Methods

The TiO_2 nano-powder was synthesized using a flat-flame chemical vapor condensation (FFCVC) method, and the complete system set-up was as described in our previous study [23]. Titanium isopropoxide (TTIP) was used as the precursor, and the carrier gas was argon. The precursor feed rate into the chamber was controlled by adjusting the flow rate of the carrier gas (argon). Nitrogen gas was used as the chamber quench gas, flowing through another pipe into the chamber, and the sources of fuel and oxidizer were acetylene and oxygen. The precursor (TTIP) was delivered into the chamber and mixed with the fuel gas through the burner. The TiO_2 nano-powder was formed in the flame through combustion.

The flow rates of acetylene (C_2H_2) were 600 sccm and 800 sccm (sccm stands for cubic centimeters per minute at standard temperature and pressure (STP)), respectively. The acetylene/oxygen flow ratios ($\text{C}_2\text{H}_2/\text{O}_2$) were 1:3, 1:4, 1:5, and 1:6. All of the nano-powder samples were prepared with a precursor carrier gas flow rate of 100 sccm, the precursor was held warm at 70 °C, the burner-to-substrate gap was 35 mm, and the pressure of the chamber was controlled at 20 torr.

The θ – 2θ scan measured the X-ray diffraction (XRD) spectra with a Cu $K\alpha$ X-ray source (Rigaku D/MAX-2500 V, 40 kV, 100 mA). The UV–visible spectra were measured using a Hitachi 3300 H. The photocatalytic activity was accessed by degradation of methylene blue under visible light using a PL lamp (PHILIPS 36W/865/4P). Methylene blue solution was prepared by dissolving 10 mg of methylene blue in 1 L of deionized water. Then, 200 mL of the methylene blue solution was taken in a 500 mL beaker with the addition of 10 mg of the TiO_2 powder under study. The beaker was then placed under the lamp with constant magnetic stirring to induce photocatalytic degradation of methylene blue. Each one hour, 3 mL of methylene blue solution was taken and measured via UV–vis absorption spectroscopy. An X-band Bruker EMX was used to measure the EPR spectra.

3. Results and Discussion

Figure 1 shows the respective XRD spectra of the TiO_2 powders synthesized by the FFCVC method with two acetylene flow rates of 600 and 800 sccm. Figure 1a shows the X-ray diffraction spectra corresponding to an acetylene flow rate of 600 sccm. The main diffraction peak appears at $2\theta = 25.3^\circ$, attributed to anatase (101), and there is a tiny rutile peak at 27.5° corresponding to rutile (110), found only in the sample at C_2H_2 600 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:3$.

In Figure 1b, for an acetylene flow rate of 800 sccm, a diffraction peak appearing at $2\theta = 25.3^\circ$ was observed for the samples at $\text{C}_2\text{H}_2/\text{O}_2 = 1:4$, $1:5$, and $1:6$, and the rutile peak did not appear for C_2H_2 800 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:3$. Besides this, the higher the flow rate of oxygen, the stronger the intensity of the rutile peak at 27.5° . The main rutile peaks appearing in spectra for samples from C_2H_2 800 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:4$ through C_2H_2 800 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:6$ have the same characteristics in terms of narrow rutile peak shape at 27.5° .

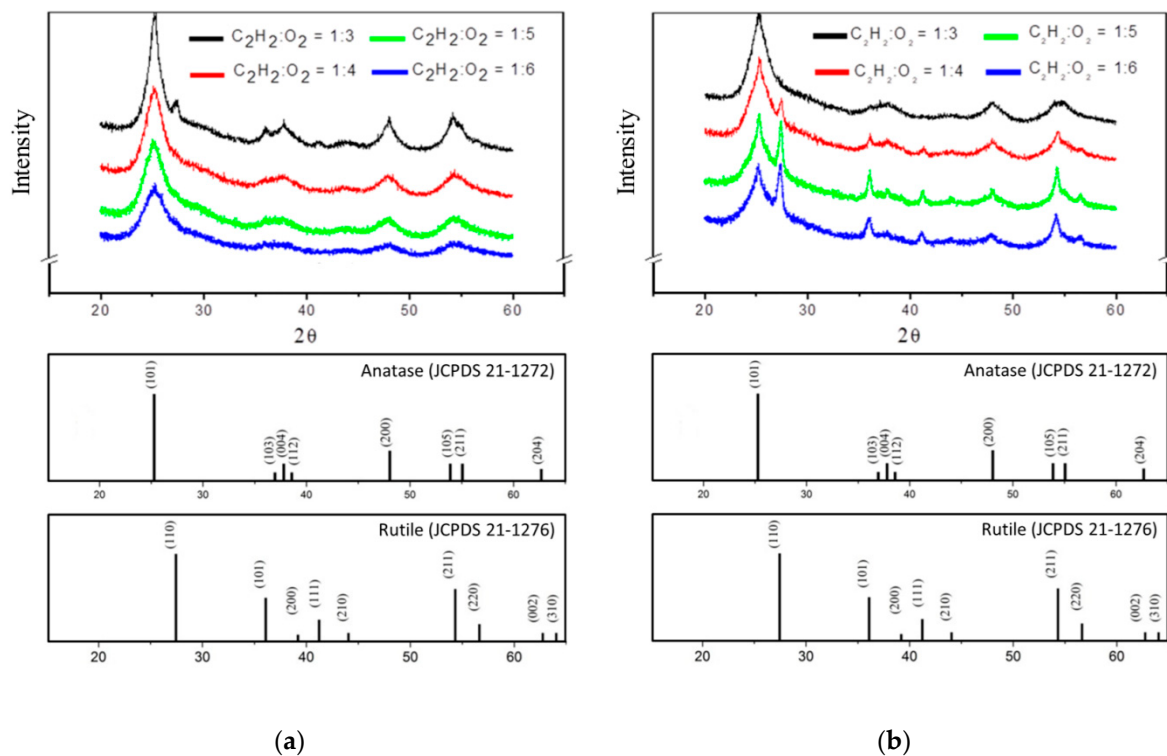


Figure 1. XRD spectra of TiO_2 powders produced by a flat-flame chemical vapor condensation (FFCVC) method using various acetylene/oxygen flow ratios ($\text{C}_2\text{H}_2/\text{O}_2$). The acetylene flow rates (C_2H_2) are (a) C_2H_2 600 sccm and (b) C_2H_2 800 sccm.

When comparing Figure 1a,b, the acetylene/oxygen flow ratios are the same. For acetylene flow of 800 sccm, the intensity of the rutile diffraction peak gets stronger as the flow rate of oxygen increases (Figure 1b). However, this trend is reversed for 600 sccm (Figure 1a). Figure 1a has almost the opposite tendency to Figure 1b in terms of rutile formation with acetylene/oxygen flow rate and, accordingly, with the oxygen flow rate.

Table 1 shows the grain sizes of anatase and rutile for all the samples prepared under different processing conditions. Scherrer's equation ($d = 0.9\lambda/\beta\cos\theta$) was used to calculate the grain size d by measuring the peak broadening β of the FWHM of the peak. The particle size of rutile is much larger than that of anatase, especially for the set of samples with an acetylene flow rate of 800 sccm.

Table 1. The grain sizes of anatase and rutile under various processing conditions.

$\text{C}_2\text{H}_2/\text{O}_2$	600 sccm				800 sccm			
	Anatase		Rutile		Anatase		Rutile	
	β	d (nm)	β	d (nm)	β	d (nm)	β	d (nm)
1:3	1.3	6.5	0.63	13.5	1.9	4.5	-	-
1:4	2.1	4.1	-	-	2.2	3.9	0.3	28.5
1:5	2.5	3.4	-	-	1.9	4.5	0.3	28.5
1:6	2.6	3.3	-	-	1.9	4.5	0.4	21.4

For the set of samples with an acetylene flow rate of 600 sccm, the grain size of rutile is small and is comparable with that of anatase, although it may have a slightly larger value. This suggests that the rutile growth is largely limited. The sub-Lorentzian-like shape of the rutile peak suggests that the population of rutile grains with size less than the average rutile grain size is low. Since the average rutile particle size is still slightly larger than that of anatase, rutile should form through transformation from anatase aggregates composed of only a few anatase grains.

Figure 2 shows the TEM micrograph and diffraction patterns of a sample with C_2H_2 800 sccm, $C_2H_2/O_2 = 1:5$. The ring pattern is diffuse and is from the anatase phase, suggesting that the anatase particle size is small. There are scattered diffraction spots not falling within the rings, which come from the rutile phase. Single-crystal diffraction on large particles was also examined (not shown) and confirmed that the crystal was rutile. This is the typical TiO_2 morphology produced at an acetylene flow rate of 800 sccm, where rutile has a much larger size than most anatase, which agrees well with the grain size deduced from the X-ray diffraction patterns.

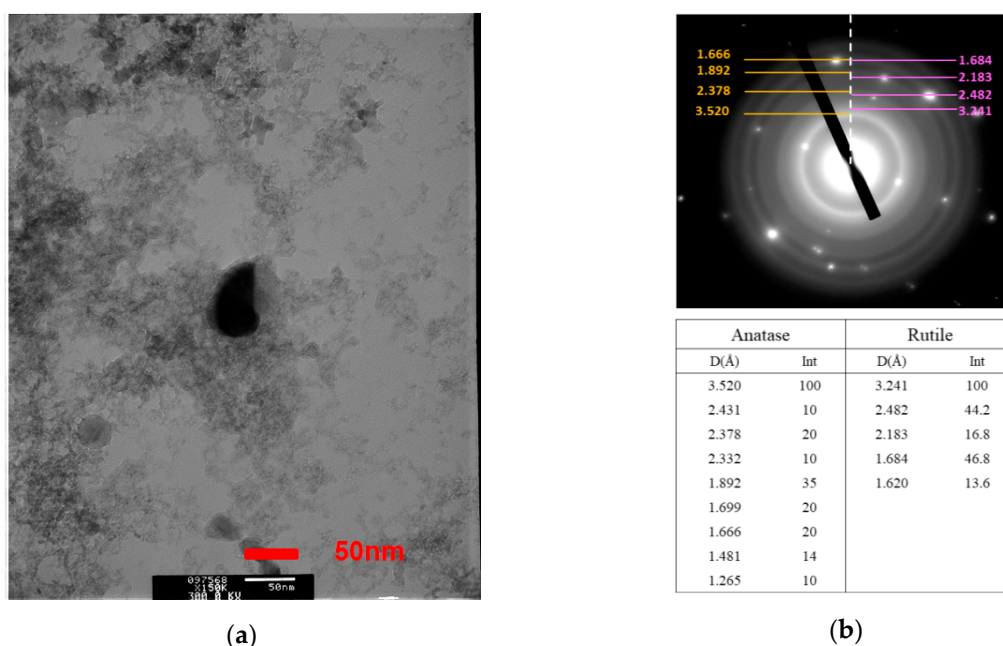


Figure 2. A typical TEM micrograph and corresponding diffraction pattern of a sample with C_2H_2 800 sccm, $C_2H_2/O_2 = 1:5$. (a) Micrograph; (b) diffraction pattern.

3.1. Rutile Formation Mechanisms

As reported, the formation of rutile has two kinds of mechanisms. One is that rutile can even form readily after its nucleation in an oxygen-deficient environment [24]. This mechanism is related to the packing of the octahedral structure of the TiO_6 unit [25]. It is known that more octahedra connect to each other by corner-sharing in rutile than in anatase, while more octahedra connect by edge-sharing in anatase than in rutile, where edge- and corner-sharing are illustrated in Figure 3. If one oxygen atom is missing in two edge-shared octahedra, the shared edge may be unlocked and form a corner-shared structure (Figure 3b). The corner-shared octahedra allow a greater degree of freedom in the tilt and rotation of octahedron concerning each other, thus providing a better chance of packing themselves from a more loosely packed anatase structure to a more densely packed, yet stable, rutile structure. The alignment of octahedra by corner-sharing is promoted in an oxygen-deficient environment; hence, rutile nucleation is enhanced in an oxygen-deficient environment. Thus, the formation of rutile by nucleation is developed in an oxygen-deficient climate, and the rutile grain size can be tiny in an oxygen-deficient environment. Another mechanism for rutile formation is through the aggregation of anatase grains to form a specific critical size (>15 nm) for triggering phase transformation from anatase to rutile at high temperatures (usually greater than $600^\circ C$). Under this condition, the grain size of rutile is larger than 15 nm [26–29], bigger than the grain size of rutile formed via the previous mechanism. According to Scherrer's equation ($d = 0.9\lambda/\beta\cos\theta$) [30], it is known that the crystallite size can be determined from the full width at half-maximum (FWHM) of XRD peaks. The diffraction peaks become broader; the grain size of the particle becomes smaller. In Figure 1b, it can be seen clearly that the rutile peak at 27.5° is sharp and narrow compared with the anatase peak at 25.3° , indicating

that the rutile grains are much larger than the anatase grains. As a result, it can be concluded that the rutile phase in the mixed powder is formed through the latter mechanism for an acetylene flow rate of 800 sccm. On the contrary, if the rutile were to form through nucleation in an oxygen-deficient environment, the rutile grains would be small, comparable with the grain size of anatase.

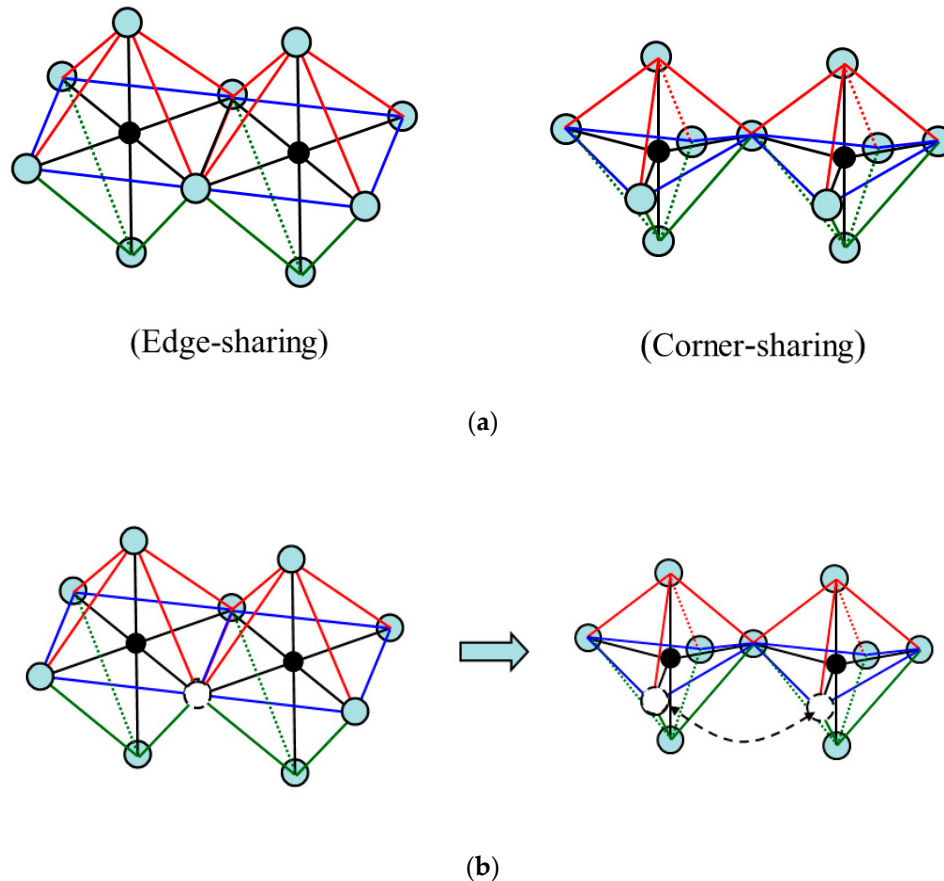


Figure 3. (a) Schematics of edge-sharing and corner-sharing of two TiO_6 octahedra. (b) The transformation of TiO_6 octahedra from corner-sharing to edge-sharing when one oxygen atom along the shared edge is missing.

As discussed earlier, the formation of rutile is related to the acetylene flow rate of 800 sccm; in this experiment, acetylene acts as the fuel for the combustion. When more acetylene flows into the chamber, more heat is created to induce the combustion reaction to form TiO_2 nanoparticles with mixed-phase anatase and rutile. Thus, the rutile formation was more pronounced in the samples with an acetylene flow rate of 800 sccm than in those with 600 sccm. The increasing trend of rutile formation with oxygen flow rate for the set of samples with an acetylene flow rate of 800 sccm should not be due to increased temperature of the flame because the stoichiometric ratio of oxygen to acetylene for the full combustion of acetylene is 2.5, and excess oxygen flow higher than this stoichiometric ratio reduces the flame temperature. Thus, the enhancement of rutile with the oxygen flow rate should be attributed to the increased aggregation or growth of anatase grains due to the increased oxygen partial pressure.

There were different trends of rutile formation with acetylene flow rates of 600 sccm and 800 sccm. In the case of 600 sccm, the temperature was insufficient for anatase-to-rutile phase transformation from large anatase aggregates; the observation that rutile formation only occurred at an acetylene/oxygen flow ratio of 1:3 for the acetylene flow rate of 600 sccm may be due to either the slight temperature increase when the acetylene/oxygen flow ratio approaches the stoichiometric ratio for full combustion or the oxygen-deficient environment caused by the reduction of oxygen flow, considering that the precursor also consumes oxygen during combustion, along with the acetylene. The oxygen-deficient environment

does help rutile formation, through either direct nucleation from the gas phase, or transformation from small anatase aggregates less than the critical size, or both.

3.2. Visible-Light Absorption

Figure 4a,b shows the UV–visible absorption spectra of the sets with C_2H_2 flow rates of 600 sccm and 800 sccm, respectively, prepared by FFCVC. The anatase-to-rutile ratio (A:R) is also provided from estimation of the areas under the X-ray diffraction peak at 25.3° (anatase (101)) and under the peak at 27.5° (rutile (110)) from a previous study. All of these powder samples absorbed visible light in the range of 380–600 nm. In Figure 4a, it can be clearly seen that the visible-light absorption ability for samples decreases in the following order: C_2H_2 600 sccm, $C_2H_2/O_2 = 1:4$; C_2H_2 600 sccm, $C_2H_2/O_2 = 1:5$; C_2H_2 600 sccm, $C_2H_2/O_2 = 1:6$; and C_2H_2 600 sccm, $C_2H_2/O_2 = 1:3$, as the arrow indicates. The visible-light absorption for sample $C_2H_2/O_2 = 1:3$ is considerably much lower than that of the other samples. In Figure 4b, all four lines almost overlap one another, but they still follow the decreasing order through the sequence of C_2H_2 800 sccm, $C_2H_2/O_2 = 1:6$; C_2H_2 800 sccm, $C_2H_2/O_2 = 1:5$; C_2H_2 800 sccm, $C_2H_2/O_2 = 1:4$; and C_2H_2 800 sccm, $C_2H_2/O_2 = 1:3$, where the sample at C_2H_2 800 sccm, $C_2H_2/O_2 = 1:6$ showed slightly stronger absorption than other three samples. The visible light absorption levels for C_2H_2 800 sccm, $C_2H_2/O_2 = 1:3$; C_2H_2 800 sccm, $C_2H_2/O_2 = 1:4$; C_2H_2 800 sccm, $C_2H_2/O_2 = 1:5$; and C_2H_2 800 sccm, $C_2H_2/O_2 = 1:6$ are comparable with, if not higher than, that for C_2H_2 600 sccm, $C_2H_2/O_2 = 1:4$, which had the highest visible-light absorption for the acetylene flow rate of 600 sccm.

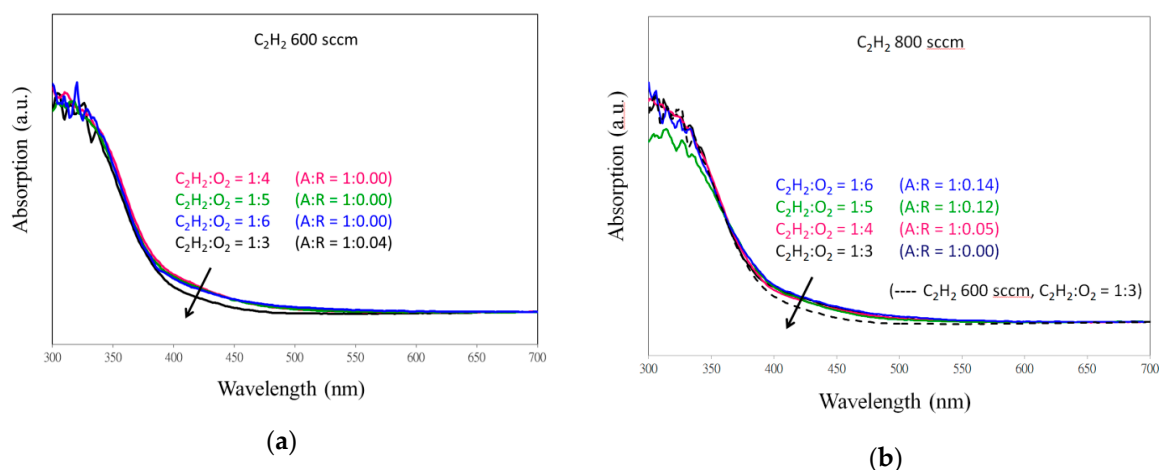


Figure 4. UV–visible absorption spectra of TiO_2 powders produced by the FFCVC method with (a) C_2H_2 600 sccm and with (b) C_2H_2 800 sccm. The dashed line provided in (b) is the spectrum for the sample with C_2H_2 600 sccm, $C_2H_2/O_2 = 1:3$, for comparison purposes. The anatase-to-rutile ratio (A:R) is also indicated.

In our previous study [26], the visible-light absorption by TiO_2 nanopowders produced by FFCVC was due to a carbon-doping-related effect. In this study, we wanted to verify whether the anatase/rutile formation resulted in a different conclusion, because the anatase/rutile interface may also create a new energy level between the valence band and conduction band edges of TiO_2 and cause visible light absorption [31–33]. Figure 5 shows the EPR spectra of all samples under visible-light illumination. The main signal appears at $g = 2.003$. Comparing Figures 4 and 5, it can be seen that for samples with higher absorption ability in the UV–vis spectra, the signal is generally stronger in the EPR spectra under illumination. Hence, the UV–vis spectral result correlates well with the EPR signal at $g = 2.003$. The signal under illumination is much stronger than that in the dark (not shown), where the weak signals of the EPR spectra in the dark do not correlate with visible-light absorption. The significant EPR signal increase due to visible-light illumination suggests that the EPR signal at $g = 2.003$ represents the photonic center for visible-light absorption. Since the illumination response is the same, and the

position of the signal is the same as that mentioned in our previous study [26], we conclude that the photonic center responsible for the visible-light absorption in this study is the same as those defects related to the carbon doping effect for the TiO_2 nanopowder mentioned in the previous study. The weak EPR signal and visible-light absorption for the sample with C_2H_2 600 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:3$ suggests that the visible-light-absorbing photonic centers are annihilated with the formation of rutile.

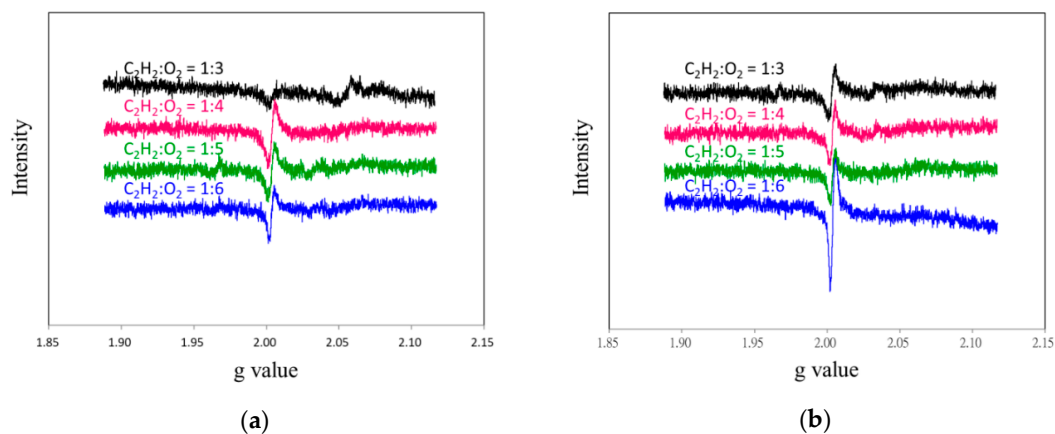


Figure 5. EPR spectra of visible-light-illuminated TiO_2 powders produced by the FFCVC method with (a) C_2H_2 600 sccm and with (b) C_2H_2 800 sccm.

3.3. Visible-Light Photocatalytic Reactivity

Figure 6 shows the degradation of methylene blue as a function of reaction time by the samples under visible light illumination. The dashed lines represent the degradation of methylene without the presence of TiO_2 powders, suggesting that photolysis of methylene blue can be neglected for the 5 h period of time examined. As can be seen from Figure 6a, samples with a single anatase phase such as C_2H_2 600 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:4$; C_2H_2 600 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:5$; and C_2H_2 600 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:6$ appear to have poor photocatalytic activity for methylene blue degradation. C_2H_2 600 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:3$, the only sample with mixed phase prepared under a C_2H_2 flow of 600 sccm, shows the highest photocatalytic activity among the samples. Figure 6b shows that for the samples with an acetylene flow rate of 800 sccm, the photocatalytic methylene blue degradation ability is significantly higher than for those with an acetylene flow rate of 600 sccm, and this ability increases with the oxygen flow rate.

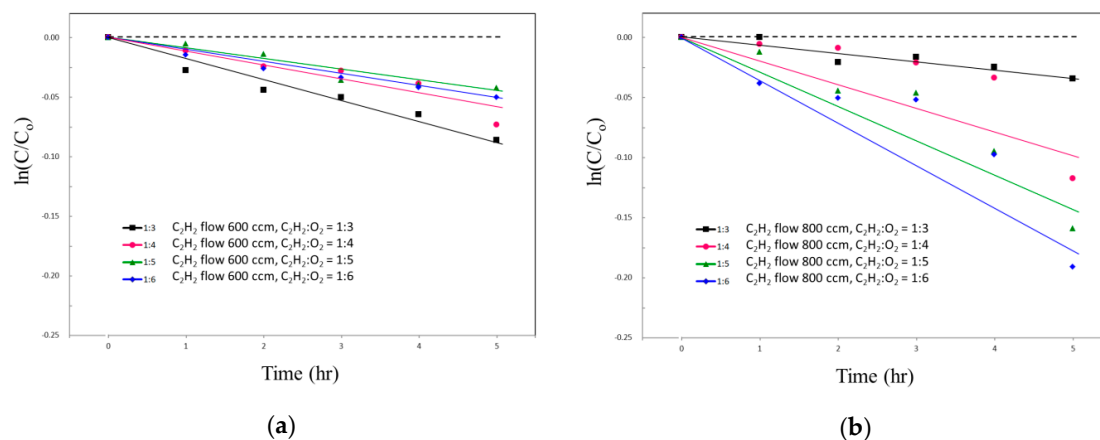


Figure 6. The degradation of methylene blue by TiO_2 powders under visible light for powder produced with (a) C_2H_2 600 sccm and with (b) C_2H_2 800 sccm. The dashed lines represent the degradation of methylene without the presence of TiO_2 powders.

As discussed earlier, the EPR signals relate to the UV–visible absorption spectra. The higher the intensity of the signal in EPR, the stronger the absorption of visible light, such as that of C_2H_2 600 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:4$ with the highest light absorption and EPR signal in Figures 4a and 5a and that of C_2H_2 800 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:6$ with the highest light absorption and EPR signal in Figures 4b and 5b. However, good absorption of visible light does not necessarily ensure good photocatalytic ability, as can be seen from Figures 4a and 6a, in which the sample with C_2H_2 600 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:4$ has the strongest absorption of visible light among the four samples prepared under an acetylene flow rate of 600 sccm, but shows a poor result of methylene blue degradation under visible light. On the other hand, the sample with C_2H_2 600 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:3$ has the weakest light absorption ability but shows the best degradation activity against methylene blue among the samples in the set for acetylene flow of 600 sccm. Recall that the sample with C_2H_2 600 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:3$ is the only sample which has rutile formation coexisting with anatase in the set with C_2H_2 flow of 600 sccm. Apparently, the anatase/rutile interface in C_2H_2 600 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:3$ does play an important role in the enhancement of the photocatalytic reaction. Note that the rutile formation is at the expense of visible-light absorption. Hence, the significant role of the anatase/rutile interface in this study is electron–hole separation instead of photonic center creation for visible-light absorption.

3.4. Photonic Center for Visible-Light Absorption

The interesting phenomenon that the rutile formation is at the expense of visible-light absorption is worth noticing. In the set with acetylene flow of 600 sccm, as the oxygen flow rate reduces to approach $\text{C}_2\text{H}_2/\text{O}_2 = 1:3$, rutile forms and is accompanied by a significant reduction of light absorption. This experiment was repeated many times and confirmed that the onset of rutile formation always coincides with a substantial decrease in light absorption for acetylene flow of 600 sccm. Thus, we claim that the visible-light-absorbing photonic center acts as the nucleation site for rutile formation for acetylene flow of 600 sccm, such that the rutile formation accompanies the elimination of the visible-light-absorbing photonic center. Furthermore, since rutile formation reduces the visible-light absorption, the visible-light-incorporating photonic center should locate neither at the anatase/rutile interface nor in rutile grains, but in anatase grains. This agrees well with our previous study that single-phase anatase TiO_2 photocatalyst prepared by FFCVC can absorb visible light while showing poor photocatalytic ability.

For the samples prepared with an acetylene flow rate of 800 sccm, rutile formation is not at the expense of the photonic center. For example, C_2H_2 800 sccm, $\text{C}_2\text{H}_2/\text{O}_2 = 1:6$ forms rutile (Figure 1b) without compromised visible-light absorption (Figure 4b); the rutile formation under elevated temperature and sufficient oxygen availability is through phase transformation from anatase aggregates and not through nucleation from the photonic center. Thus, the remaining anatase may still possess the photonic center for visible light absorption for samples prepared under acetylene flow of 800 sccm. As discussed before, the formation of rutile by nucleation is feasible in an oxygen-deficient environment even when the temperature is not high enough for rutile formation by phase transformation from large anatase aggregates (>15 nm). Oxygen vacancy should play a vital role in the unlocking of the edge-sharing octahedra towards corner-sharing octahedra, which leads to rutile nucleation. In light of the finding that the visible-light-absorbing photonic center acts as the nucleation site for rutile formation for acetylene flow of 600 sccm, the visible-light-incorporating photonic center should be closely related to the defect of oxygen vacancy on the surface of anatase grains. The literature suggests that the defect level of oxygen vacancy in anatase lies 0.75 eV–1.18 eV below the conduction band edge of anatase. The defect level described above agrees quite well with our visible-light absorption spectrum starting from the lowest photonic energy with an equivalent wavelength around 600 nm. Thus, the visible-light absorption by our samples should yield electron excitation from the valance band edge to the defect level of oxygen vacancy in anatase.

A schematic energy band diagram is required, shown in Figure 7, for the anatase/rutile photocatalyst prepared by the FFCVC process to illustrate the possible electron flow direction and to

highlight the role of the anatase/rutile dual-phase structure in enhancing photocatalytic activity under visible light illumination. The anatase and rutile were aligned following the consensus suggested in the literature that the conduction band edge has about 0.2 eV offset. In contrast, the valance band edges of anatase and rutile are close to each other. Recall that the defect level of the photonic center is located on the anatase side. When visible light illuminates the nanopowder prepared with C_2H_2 600 sccm, $C_2H_2/O_2 = 1:3$, there is little visible-light absorption, and the electron–hole pair cannot be formed by visible-light illumination, as shown in Figure 7a. When visible light illuminates the nanopowder with significant visible-light absorption, the electrons are excited to the defect energy level in anatase, as shown in Figure 7b. Since the defect levels are lower than the conduction band edge of rutile, most of the electrons cannot overcome the energy barrier of rutile and are forced to flow away from the anatase/rutile interface. Thus, those electrons attempting to flow towards rutile are mainly turned away by the interface so as to reduce electron–hole recombination on the rutile side. The holes on the rutile side are mostly free from recombination with electrons and are allowed to proceed with their photocatalytic reaction on the rutile surface. With the help of the anatase/rutile interface, the particles generated on anatase are separated from rutile effectively, and the visible-light photocatalytic activity of the TiO_2 nanopowder is enhanced.

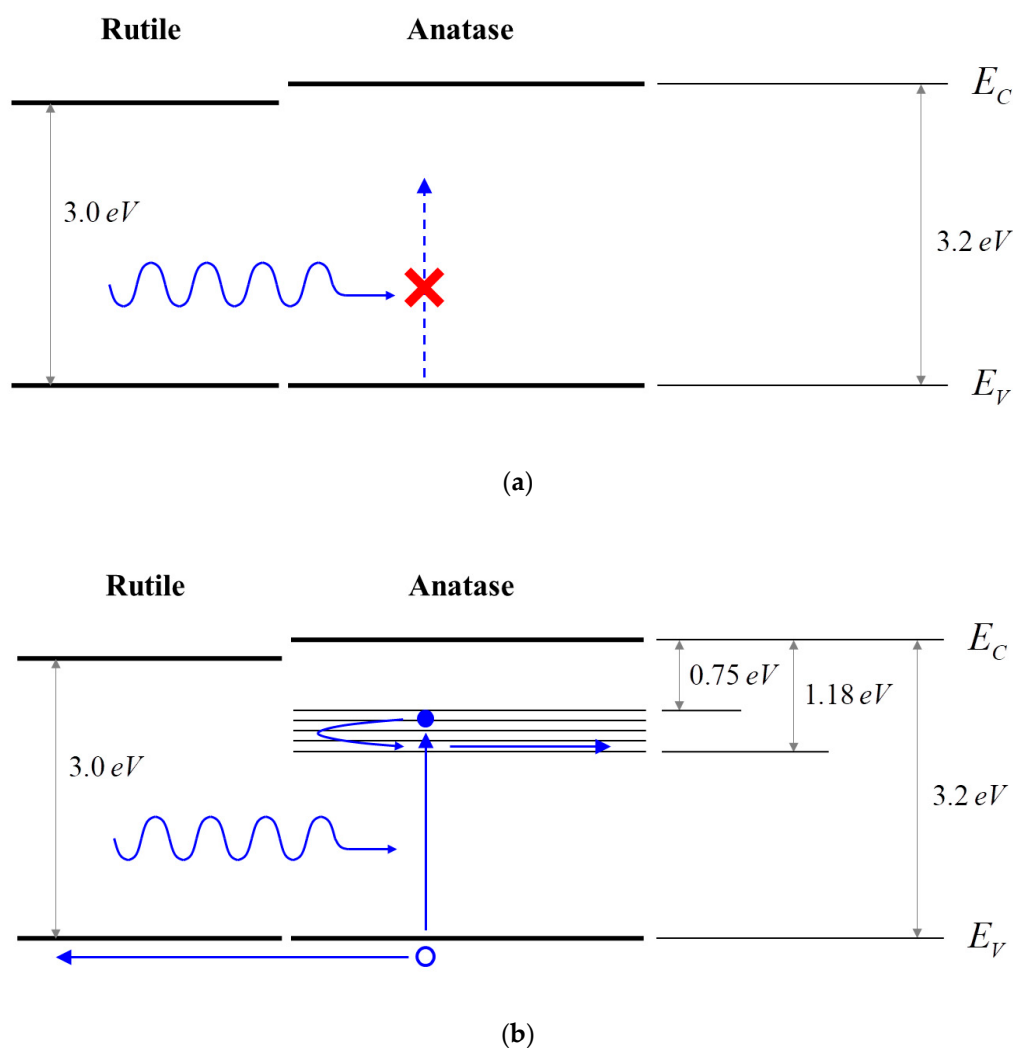


Figure 7. A schematic diagram of photoelectron generation and movement in TiO_2 with an anatase/rutile interface under visible light illumination (a) without a visible-light-absorbing photonic center and (b) with a visible-light-absorbing photonic center.

4. Conclusions

We successfully enhanced the visible-light photocatalytic activity of TiO₂ powder by rutile formation using an FFCVC process. The rutile formation for TiO₂ prepared under acetylene flow of 800 sccm occurs through phase transformation from anatase aggregates, while the rutile formation for TiO₂ prepared under acetylene flow of 600 sccm is mainly through nucleation from the photonic center. The photonic center for visible-light absorption is located on the anatase side. The role of the anatase/rutile dual phase in the samples is the blockage of photoelectrons by the anatase/rutile interface to suppress electron/hole recombination, not light harvesting.

Author Contributions: Y.-J.C. supervised the project and wrote the manuscript while T.-S.L. carried out the experiment. All authors have read and agreed to the published version of the manuscript.

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

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