

Article

Synthesis, Structure, and Photocatalytic Activity of TiO₂-Montmorillonite Composites

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Abstract: In the present study, TiO₂-montmorillonite (MMT) composites were synthesized hydrothermally under variable conditions, including the TiO₂/MMT mass ratio, reaction pH, reaction temperature, and dwelling time. These samples were determined by X-ray photoelectron spectrometry (XPS), ultraviolet–visible spectroscopy (UV-Vis DRS), electrochemical impedance spectroscopy (EIS), transient photocurrent responses, photoluminescence (PL) spectra, electron paramagnetic resonance (EPR), and N₂ adsorption–desorption isotherms. The photocatalytic activity was evaluated as the ability to promote the visible-light-driven degradation of 30 mg/L of aqueous methylene blue, which was maximized for the composite with a TiO₂ mass ratio of 30 wt% prepared at a pH of 6, a reaction temperature of 160 °C, and a dwelling time of 24 h (denoted as 30%-TM), which achieved a methylene blue removal efficiency of 95.6%, which was 4.9 times higher than that of pure TiO₂. The unit cell volume and crystallite size of 30%-TM were 92.43 Å³ and 9.28 nm, respectively, with a relatively uniform distribution of TiO₂ particles on the MMT's surface. In addition, 30%-TM had a large specific surface area, a strong light absorption capacity, and a high Ti³⁺ content among the studied catalysts. Thus, the present study provides a basis for the synthesis of composites with controlled structures.

Keywords: hydrothermal synthesis; TiO₂-montmorillonite; photocatalysis; synthetic conditions



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1. Introduction

The global energy crisis and environmental pollution have necessitated the development of materials that can reduce our dependence on nonrenewable energy sources and remove hazardous pollutants from wastewater [1–5]. Recently, photocatalytic degradation has attracted significant attention as a novel, simple, and environmentally friendly wastewater treatment method, which is superior to traditional techniques that rely on adsorption, membrane separation, ion exchange, and oxidation [6–9]. Titanium dioxide is extensively used for the photocatalytic degradation of pollutants owing to its nontoxicity, low cost, high chemical stability, hydrophilicity, and good catalytic activity [10,11]. However, it exhibits certain drawbacks, such as rapid electron–hole recombination and a wide band gap [12].

Montmorillonite (MMT) is a common lamellar aluminosilicate [13] that is often used as a photocatalyst support owing to its large specific surface area [10], its high adsorption capacity for cations and polar molecules [14], and stable chemical properties [15]. Composites of TiO₂-MMT have been reported to exhibit slower electron–hole recombination and promote better oxidative degradation of pollutants by ozone compared with pure TiO₂ and MMT [16]. The porosity of these composites, prepared by reacting titanium

silicalite with titanium alkoxides at 50–80 °C, strongly influences their ability to adsorb dyes such as methylene blue (MB), which can be adjusted by varying the reaction temperature [17]. A study reporting the preparation of TiO₂ gel from titanium tetrachloride (TiCl₄) at 30–80 °C demonstrated the photocatalytic performance of the resulting TiO₂-MMT composite, which was maximized at a reaction temperature of 70 °C [18]. In another study, TiO₂-MMT suspensions were hydrothermally prepared from titanium sulfide (Ti(SO₄)₂) and MMT at pH 4, and calcined for 2 h at 300–1200 °C [10]. The growth of anatase and rutile TiO₂ was inhibited by adding MMT, while the complete transformation of anatase TiO₂ into rutile TiO₂ was observed at 900 °C. TiO₂-MMT composites prepared by combining cation filling, sol-gel processing, and thermal treatment featured a narrow band gap of 2.79 eV and advantageous structural properties [19]. Preparation of a carbon-modified nitrogen-doped TiO₂/montmorillonite composite by the sol-gel method increased the absorption range of light and realized the effective separation of photogenerated electron pairs [20]. Mohammad et al. prepared a kind of gray titanium dioxide, which increased the content of Ti³⁺ and oxygen vacancies in titanium dioxide and increased the rate of charge transfer [21]. Yusuke et al. studied the synergistic effect of layered silicate and TiO₂ on the photocatalytic oxidation of benzene to recover phenol with unprecedented efficiency and selectivity [22].

More recently, TiO₂-MMT composites were shown to exhibit high photocatalytic activity even at elevated temperatures, which was ascribed to the presence of TiO₂ in the anatase phase [16,17,23,24]. Esmail et al. reported a Cl-doped rutile titanium dioxide photocatalyst, which alone could produce a lower effective carrier mass, higher photogenerated electron and hole mobility, and a longer Ti³⁺ ion interaction lifetime, thus improving the photocatalytic activity [25]. Compared with pure TiO₂, TiO₂-MMT composites are easier to recover, facilitating their industrial applications [26], and can exhibit reduced absorbance at 220–300 nm [27].

Numerous studies have probed the effects of the photodegradation conditions (such as solution pH, initial dye concentration, reaction atmosphere, and illumination time) on the photocatalytic performance of TiO₂-MMT composites [10,16,27–29]. However, only a few have examined the corresponding effects of composite preparation conditions, such as the TiO₂/MMT mass ratio and pH of the hydrothermal reaction, which may affect the structure and properties of the composite (for example, the phase composition, chemical bonding, the absorption range, and energy bands), thereby influencing the photocatalytic performance. Herein, we hydrothermally synthesized pure TiO₂ and TiO₂-MMT composites. We examined the effect of TiO₂ content, reaction pH, reaction temperature, and dwelling time on the ability of these composites to promote the photodegradation of MB, which was compared with that of pure TiO₂ and MMT. Through detection and analysis by X-ray photoelectron spectrometry (XPS), ultraviolet–visible spectroscopy (UV), electrochemical impedance spectroscopy (EIS), transient photocurrent responses, photoluminescence (PL) spectra, electron paramagnetic resonance (EPR), and Brunner–Emmet–Teller measurements (BET), the materials with the best properties under different conditions were explored. Thus, this study describes valuable correlations between synthetic conditions and catalyst properties, and thus provides a basis for synthesizing composites with a controlled structure.

2. Results and Discussion

2.1. Structural, Morphological, and Chemical Bonds

Figures 1 and 2 illustrate the XRD patterns of TiO₂-MMT composites prepared under different conditions, demonstrating peaks at $2\theta = 25.3^\circ, 37.8^\circ, 48.1^\circ, 53.9^\circ, 55^\circ$, and 62.8° that correspond to the (101), (004), (200), (105), (211), and (204) planes of anatase (JCPDS NO.73-1764), respectively. Notably, the anatase (101) surface had a higher intrinsic photocatalytic activity compared with other TiO₂ crystal faces [24]. The peak corresponding to the (101) plane was the most intense among those observed previously [28], with the variation in its intensity reflecting the effect of the MMT addition and reaction conditions on the crystallization state of TiO₂ and thereby on the photocatalytic performance. Apart from

anatase and MMT, the XRD patterns featured relatively sharp peaks of quartz, indicating a large surface area owing to the flaky structure of MMT.

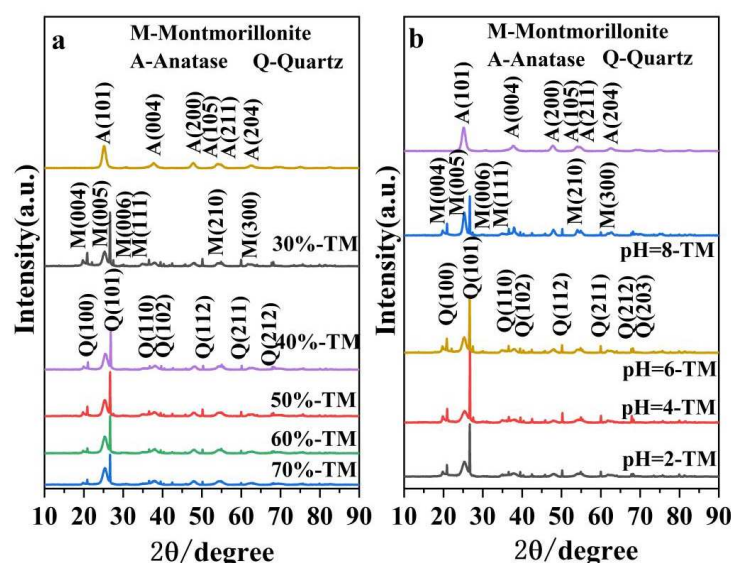


Figure 1. X-ray diffraction patterns of TiO₂-montmorillonite (MMT) composites prepared using (a) different TiO₂/MMT mass ratios at a reaction temperature of 160 °C, a dwelling time of 24 h, and a pH of 6, and (b) different pH values at a reaction temperature of 160 °C, a dwelling time of 24 h, and a TiO₂ mass ratio of 30 wt%.

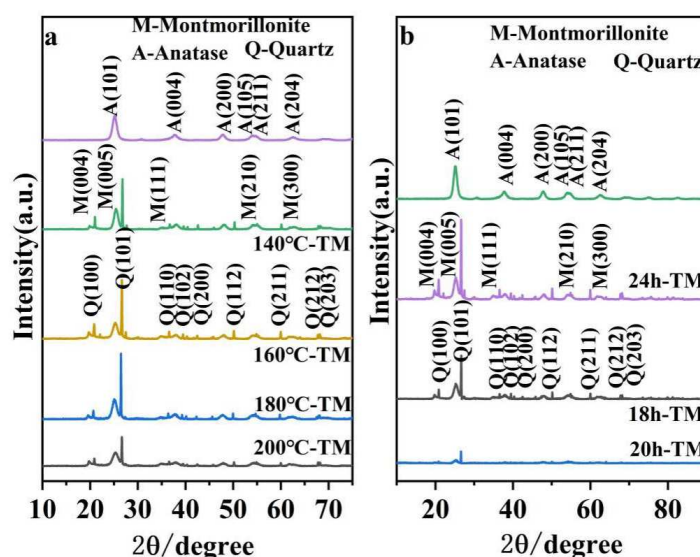


Figure 2. X-ray diffraction patterns of TiO₂-montmorillonite (MMT) composites prepared using (a) different reaction temperatures with a dwelling time of 24 h, a pH of 6, and a TiO₂ mass ratio of 30 wt%, and (b) different dwelling times at a reaction temperature of 160 °C, a pH of 6, and a TiO₂ mass ratio of 30 wt%.

Figure 1a reveals that the relative intensity of the anatase peaks, and thereby the amount of anatase, increases with an increase in the TiO₂ content; however, the intensity was less than that observed for pure TiO₂. The strongest MMT peaks indicated that the lamellar structure was best preserved at a TiO₂ mass ratio of 30 wt%. Table 1 illustrates the unit cell parameters, unit cell volumes (V), and crystallite sizes (D) of the investigated materials, which belong to the tetragonal system. The unit cell volume was calculated as $V = 0.866a^2c$ [29,30], and the crystallite size was calculated as $D = K\lambda/(\beta\cos\theta)$, where θ is the diffraction angle, β is the full width at half-maximum of the most intense peak, λ is

the X-ray wavelength (0.15406 nm), and K is the Debye–Scherrer constant (0.89) [14,31,32]. The average crystallite size of the samples described in Figure 1a first increased and then decreased with an increase in the TiO_2 content, while the maximum cell volume was obtained at a TiO_2 mass ratio of 70 wt% ($V = 117.97 \text{ \AA}^3$).

Table 1. Selected structural parameters of the prepared composites and the TiO_2 reference ($a = b \neq c$, $\alpha = \beta = \theta = 90^\circ$).

Parameters	a (Å)	b (Å)	c (Å)	V (Å ³)	D (nm)
TiO_2	3.776	3.776	7.486	92.43	9.74
30%, pH = 6, 160 °C, 24 h TiO_2 -MMT (30%-TM)	3.780	3.780	9.510	117.67	9.28
40%, pH = 6, 160 °C, 24 h TiO_2 -MMT (40%-TM)	3.776	3.776	9.486	117.13	9.28
50%, pH = 6, 160 °C, 24 h TiO_2 -MMT (50%-TM)	3.776	3.776	9.486	117.13	9.42
60%, pH = 6, 160 °C, 24 h, TiO_2 -MMT (60%-TM)	3.783	3.783	9.497	117.70	9.43
70%, pH = 6, 160 °C, 24 h TiO_2 -MMT (70%-TM)	3.784	3.784	9.514	117.97	9.24
pH = 2, 30%, 160 °C, 24 h TiO_2 -MMT (pH = 2-TM)	3.784	3.784	9.514	117.97	9.65
pH = 4, 30%, 160 °C, 24 h TiO_2 -MMT (pH = 4-TM)	3.776	3.776	9.486	117.13	9.00
pH = 6, 30%, 160 °C, 24 h TiO_2 -MMT (pH = 6-TM)	3.780	3.780	9.510	117.67	9.28
pH = 8, 30%, 160 °C, 24 h TiO_2 -MMT (pH = 8-TM)	3.785	3.785	9.785	121.40	11.76
140 °C, 30%, pH = 6, 24 h TiO_2 -MMT (140 °C-TM)	3.780	3.780	9.510	117.67	8.98
160 °C, 30%, pH = 6, 24 h TiO_2 -MMT (160 °C-TM)	3.780	3.780	9.510	117.67	9.28
180 °C, 30%, pH = 6, 24 h TiO_2 -MMT (180 °C-TM)	3.807	3.807	9.090	114.09	9.52
200 °C, 30%, pH = 6, 24 h, TiO_2 -MMT (200 °C-TM)	3.807	3.807	9.090	114.09	9.79
18 h, 30%, pH = 6, 160 °C TiO_2 -MMT (18 h-TM)	3.784	3.784	9.515	117.99	9.994
20 h, 30%, pH = 6, 160 °C TiO_2 -MMT (20 h-TM)	3.784	3.784	9.515	117.99	10.73
24 h, 30%, pH = 6, 160 °C TiO_2 -MMT (24 h-TM)	3.780	3.780	9.510	117.67	9.28

Figure 1b shows that the anatase (101) peak was the strongest and sharpest at pH 8. Thus, the sample prepared at pH 8 had the highest crystallinity. Moreover, the pH = 6-TM sample featured the strongest MMT (004), (111), (210), and (300) peaks, thus exhibiting the most preserved MMT microstructure. These results, in combination with Table 1 and Figure 2, implied that the particle size of TiO_2 in the composite became finer when TiO_2 was adsorbed on the MMT surface, which could benefit the photocatalytic performance. The weakest MMT peaks were observed for the sample prepared at pH 2, indicating that the MMT structure was largely destroyed under these conditions. The average crystallite size

of the samples described in Figure 1b first decreased and then increased with an increase in pH, while the maximum cell volume was obtained at pH 8 ($V = 121.40 \text{ \AA}^3$).

Figure 2a demonstrates that the intensities of anatase (101), MMT, and quartz peaks reached a maximum at 180°C ; the position of the anatase (101) peak was influenced by the temperature. The average crystallite size of the samples increased steadily with an increase in temperature, and the maximum cell volume was obtained at 140°C ($V = 117.67 \text{ \AA}^3$).

Figure 2b shows that the intensity of the anatase (101) peak, and thus the crystallinity and photocatalytic activity of TiO_2 , was maximum at 24 h. In addition, the intensities of quartz and MMT (004) peaks were maximized at 24 h, indicating that this dwelling time was the most suited for preserving the MMT's microstructure. In contrast, TiO_2 particle agglomeration was observed with a dwelling time of 20 h. The average crystallite size of the samples first increased and then decreased with an increase in the dwelling time, and the maximum cell volume was obtained for dwelling times of 18 and 20 h ($V = 117.99 \text{ \AA}^3$).

Figure 3 shows the SEM images of 30%-TM at different magnifications, revealing that the ordered lamellar structure of MMT remained intact after the hydrothermal reaction, and showing the presence of well-dispersed TiO_2 nanoparticles on and between the MMT layers [33]. The corresponding particle size distribution (Figure 4) suggested that the TiO_2 particles and their aggregates had sizes of 10–30 and 50–100 nm, respectively. These results implied that hybridization with TiO_2 did not destroy the ordered interlayer structure of MMT, allowing complete utilization of the large interlamellar and surface area of the latter [34].

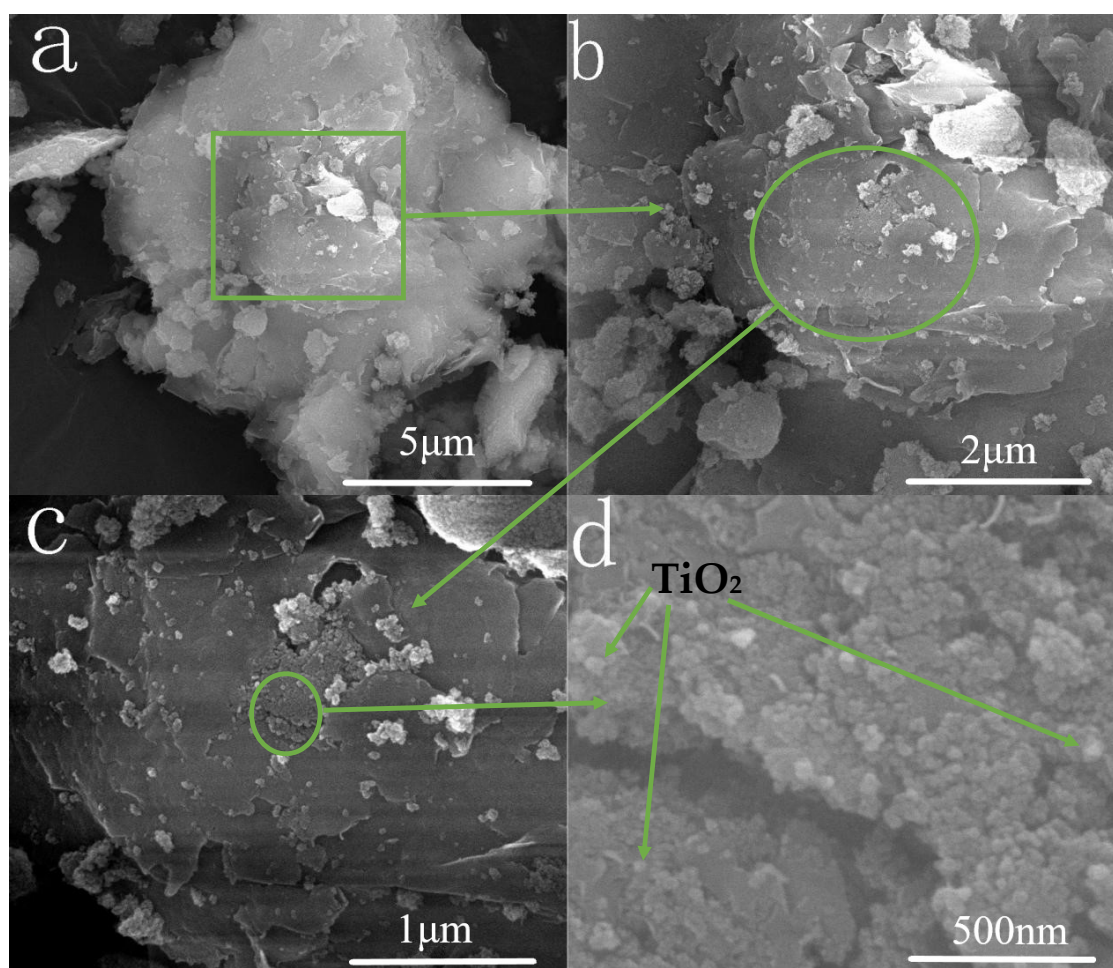


Figure 3. (a–d) Scanning electron microscopy images of 30%-TM at different magnifications.

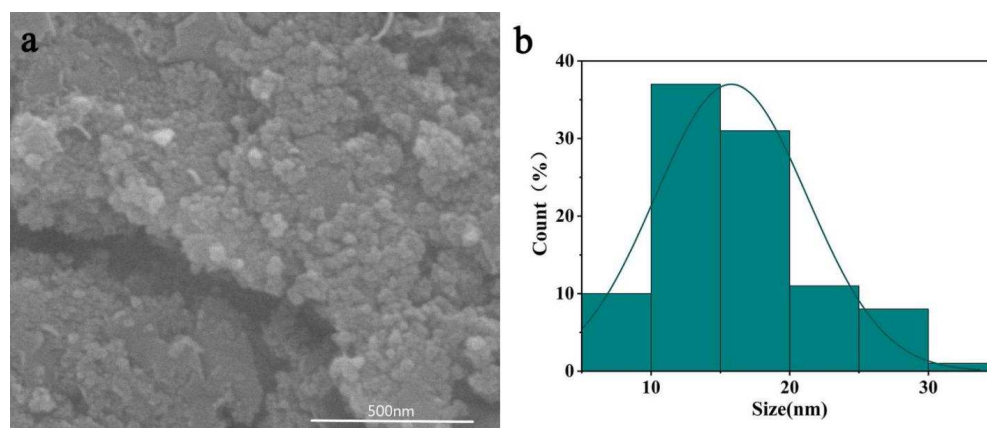


Figure 4. (a) Representative scanning electron microscopy image of 30%-TM and (b) the related size distribution of TiO_2 particles.

Figures 5 and 6 illustrate the FTIR spectra of TiO_2 -MMT composites, pure TiO_2 , and MMT. The absorption bands of pure TiO_2 were located at 480, 1345, 1377, 1594, 1630, 2821, 2921, and 3423 cm^{-1} (Figure 6a). The band at 480 cm^{-1} was ascribed to the tensile vibration of Ti–O bonds [35,36]. Peaks at 1594 and 1630 cm^{-1} were attributed to the vibration of hydroxyl and water molecular layers [32], whereas the peaks at 2821 and 2921 cm^{-1} were ascribed to the asymmetric vibration of the C–H bonds. The broad peak at 3423 cm^{-1} was assigned to the stretching vibration of hydroxyl groups, which were mainly represented by adsorbed moisture and hydroxyl groups on the TiO_2 's surface. Pure MMT featured peaks at 472, 525, 775, 1048, 1594, and 3420 cm^{-1} . The peak at 3420 cm^{-1} was due to the symmetrical O–H stretching of the absorbed moisture, whereas that at 1594 cm^{-1} was ascribed to the deformation vibration of the interlayered water molecules. The strong peak at 1048 cm^{-1} was assigned to asymmetric Si–O stretching. The signals at 775, 525, and 472 cm^{-1} were attributed to Al–O bond stretching, Al–O–Si bond deformation, and Si–O–Si bond deformation, respectively [36,37].

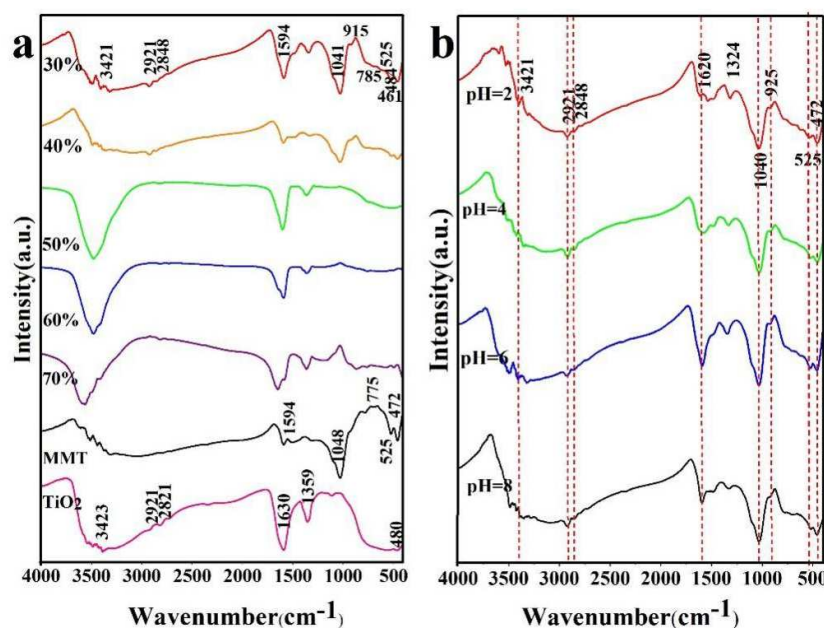


Figure 5. Fourier transform infrared spectra of TiO_2 -montmorillonite (MMT) composites prepared using (a) different TiO_2 /MMT mass ratios at a reaction temperature of 160 $^{\circ}\text{C}$, a dwelling time of 24 h, and a pH of 6, and (b) different pH values at a reaction temperature of 160 $^{\circ}\text{C}$, a dwelling time of 24 h, and a TiO_2 mass ratio of 30 wt%.

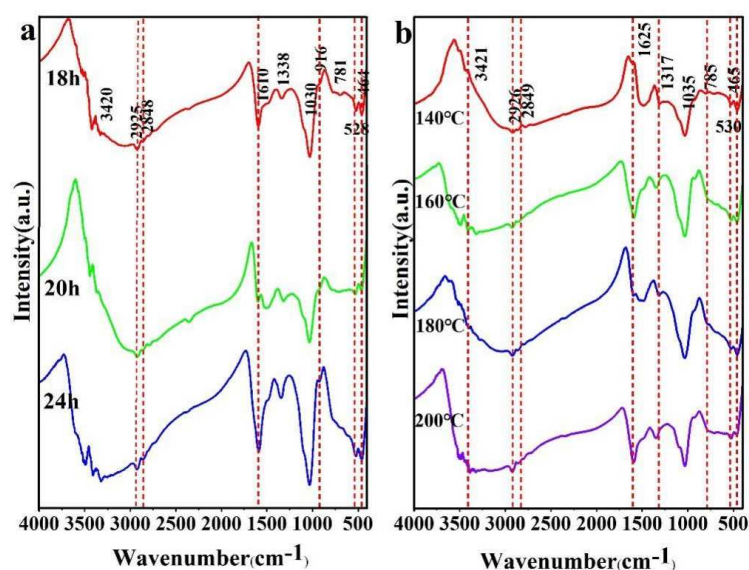


Figure 6. Fourier transform infrared spectra of TiO₂-montmorillonite (MMT) composites prepared using (a) different dwelling times at a reaction temperature of 160 °C, a pH of 6, and a TiO₂ mass ratio of 30 wt% and (b) different reaction temperatures at a dwelling time of 24 h, a pH of 6, and a TiO₂ mass ratio of 30 wt%.

The peak range of 910–930 cm^{−1} was observed only for the TiO₂-MMT composites and was assigned to the Si–O–Ti units produced from the reaction of SiO₂ with TiO₂ [31,32]. The formation of Si–O bonds increased the number of oxygen vacancies on the surface of the TiO₂ attached to the MMT [19], enhancing the catalytic performance of the composites. Figure 6a shows that the characteristic absorption band of MMT is unclear for composites with a TiO₂ mass ratio of 50, 60, and 70 wt%. This behavior could reflect the increased occurrence of the reaction of SiO₂ with TiO₂ with the increase in TiO₂ content, which decreased the intensity of the Si–O–Si deformation vibration, Al–O–Si deformation vibration, Si–O tensile vibration, and Ti–O tensile vibration. Figure 5b shows that for pH 2, no peaks were observed at 472 and 525 cm^{−1}, implying that the lamellar structure of MMT was destroyed under strongly acidic conditions, which affected the photocatalytic performance.

2.2. Photocatalytic Activity and Dye Degradation

Figure 7a shows the absorption maxima of MB at 664 nm, which decreased with the degradation time for 30%-TM. Figure 7b,c demonstrates the absorbance spectra obtained for the degradation of MB with different catalysts at degradation times of 120 and 0 min, respectively. Figure 8b illustrates insignificant changes in the absorbance of MB in the blank group (light, no catalyst), suggesting that MB is relatively stable in the absence of a photocatalyst. Figure 8a shows that pure TiO₂ had a low MB adsorption capacity in the dark and achieved a fluctuating MB removal efficiency of only 7% after 2 h. However, pure TiO₂ achieved a removal efficiency of 19.4% after 2 h when irradiated with light (Figure 8b), indicating that it exhibited a certain photocatalytic activity. In contrast, the MB removal efficiency of MMT did not depend on the lighting conditions because the dye was removed by adsorption only. Figure 8a illustrates the MB adsorption capacity of TiO₂-MMT composites, which was lower than that of the pure MMT and required more time to reach an adsorption equilibrium (70 min vs. 60 min for MMT). However, after irradiation for 2 h, a further increase in the removal efficiency was observed upon the hybridization of TiO₂ with MMT. The highest degradation efficiency of 95.6% after 2 h was observed for composites at a TiO₂ content of 30%. The degradation rate of MB by 30%-TM was superior to many of the previously reported TiO₂-based and Ag-based photocatalysts, as shown in Table 2.

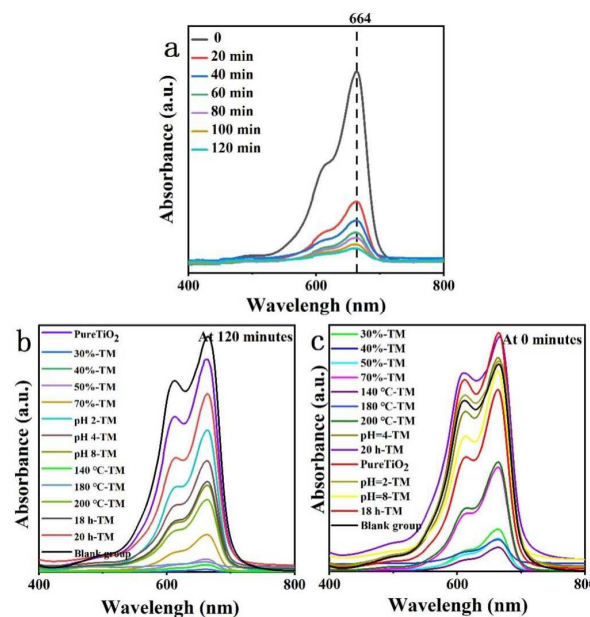


Figure 7. Ultraviolet–visible absorption spectra of methylene blue solutions degraded by (a) 30%-TM (degradation time = 0–120 min) and (b,c) TiO₂-MMT composites synthesized under different conditions (degradation time = (b) 120 min and (c) 0 min).

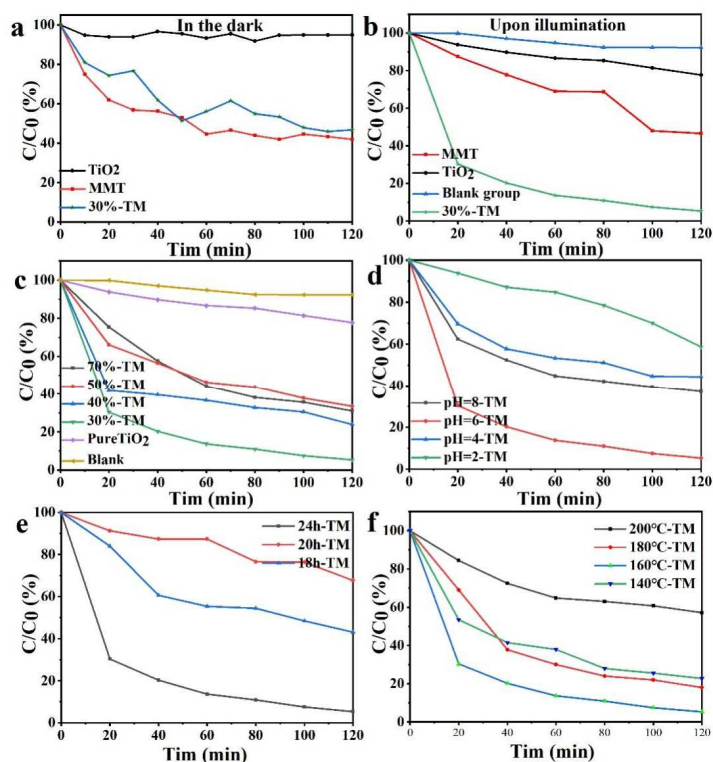


Figure 8. Methylene blue degradation curves obtained for (a) TiO₂, montmorillonite (MMT), and 30%-TM under dark conditions; (b) the blank group, TiO₂, MMT, and 30%-TM under visible light; (c) composites with different TiO₂ contents prepared at a reaction temperature of 160 °C, a dwelling time of 24 h, and a TiO₂ mass ratio of 30 wt%; (d) composites prepared at different pH values with a dwelling time of 24 h, a pH of 6, and a TiO₂ mass ratio of 30 wt%; (e) composites prepared with different dwelling times at a reaction temperature of 160 °C, a pH of 6, and a TiO₂ mass ratio of 30 wt%; and (f) composites prepared at different reaction temperatures with a dwelling time of 24 h, a pH of 6, and a TiO₂ mass ratio of 30 wt%.

Figure 8d shows the MB degradation curves for composites prepared at different pH values, revealing that the highest degradation efficiency of 76.1% after 2 h was obtained for pH 6. Although the sample prepared at pH 2 had the best absorption range and the lowest band gap, it exhibited poor photocatalytic performance. This result can be explained as follows: as a cationic dye, MB mainly exists in the cationic form at pH 8 [38]. Because the zero-charge point of TiO₂ is at pH 6.8, the surface of TiO₂ is positively charged (pH < 6.8) in acidic solutions and negatively charged (pH > 6.8) in alkaline solutions [32]. Therefore, the surface of TiO₂ particles is positively charged at pH 2. In addition, MMT mainly exists as large aggregates with a partially destroyed lamellar structure under acidic conditions (pH 1), whereas the size of these aggregates decreases at pH 7 [39]. Moreover, MMT has a negative potential, which changes insignificantly under acidic conditions. Thus, the electrostatic attraction induces the aggregation of positively charged TiO₂ with negatively charged MMT [40] to produce composites with reduced surface potential and surface area available for dye adsorption and photon absorption, thereby seriously affecting the adsorption of MB during its degradation. When hydrothermal synthesis was performed at pH 8, Coulombic repulsion existed between the negatively charged surfaces of TiO₂, MMT, and OH[−] anions. Therefore, the number of TiO₂ particles on the surface of the composite prepared at pH 8 was less than that on the surface of the composite prepared at pH 6, thereby exhibiting fewer active TiO₂ surface sites and lower performance.

Table 2. Comparison of the percentage of degradation of 30%-MT with previously reported photocatalysts.

Material	Light Source	Pollutant	% Degradation	Time (min)	Reference
CA/TiO ₂	Visible light	Methylene blue	85	300	[41]
ZnO/Ag	Visible light	Methyl orange	78	180	[42]
NiO/Ag	Visible light	Methyl orange	42	180	[42]
TiO ₂ /Ag	Visible light	Methyl orange	86	180	[42]
Cu-MOF-235	Visible light	Methylene blue	90	480	[43]
B-TiO ₂ /MIL100(Fe)	Visible light	Methylene blue	91.12	60	[44]
Cd-TCAA	Visible light	Methylene blue	81	175	[45]
ZnO-TiO ₂	Visible light	Methylene blue	62	120	[46]
TiO ₂ /Al ₂ O ₃ @Cu(BDC)	Visible light	Methylene blue	33.77	30	[47]
TiO ₂ @Ti(BTC)	Visible light	Methylene blue	56	60	[48]
30%-MT	Visible light	Methylene blue	95.6	120	This work

Figure 8e shows the effect of dwelling time, indicating that the MB degradation performance was maximized (95.6% after 2 h) and minimized (33.4% after 2 h) with dwelling times of 24 and 20 h, respectively. The overall intensity of the FTIR peaks of the sample prepared by using a dwelling time of 20 h was lower than that observed for samples with different dwelling times, which may be attributed to the agglomeration of TiO₂ particles on the lamellar structure of MMT. This agglomeration also affected the intensity of the characteristic MMT diffraction peaks, although it did not destroy the MMT's structure. This hypothesis agrees with the maximization of the average crystallite size of TiO₂ with a dwelling time of 20 h (10.73 nm).

Figure 8f illustrates the effect of the reaction temperature, exhibiting maximum (95.6%) and minimum (42.8%) MB degradation performance at 160 and 200 °C, respectively. The sample prepared at 200 °C had the largest average TiO₂ crystallite size of 9.79 nm. In contrast, the corresponding FTIR spectrum showed no new peaks, which agreed with the results of the optical band gap analysis. Therefore, the poor performance of the sample prepared at 200 °C was ascribed to the agglomeration of TiO₂ particles and the absence of heterogeneous TiO₂-MMT aggregation.

To probe the mechanism of catalytic MB degradation, we used active species trapping experiments (Figure 9). In particular, 5,5-dimethyl-pyrroline N-oxide (DMPO, a spin trapping agent) reacted with photogenerated holes (h^+) to produce the radical cation DMPO^+ , which subsequently reacted with water molecules to form $\text{DMPO-OH}^\bullet$. The signals of spin adducts were predictably weak in the dark and became more intense when irradiated with light. A typical four-line electron paramagnetic resonance (EPR) signal of $\text{DMPO-OH}^\bullet$ ($g = 2.0057$, intensity ratio = 1:2:2:1) was observed for all samples after irradiation and was more intense for TiO_2 -MMT composites than for pure TiO_2 , which implied that MMT remarkably enhanced the ability of TiO_2 to produce $\cdot\text{OH}$ radicals (Figure 9a).

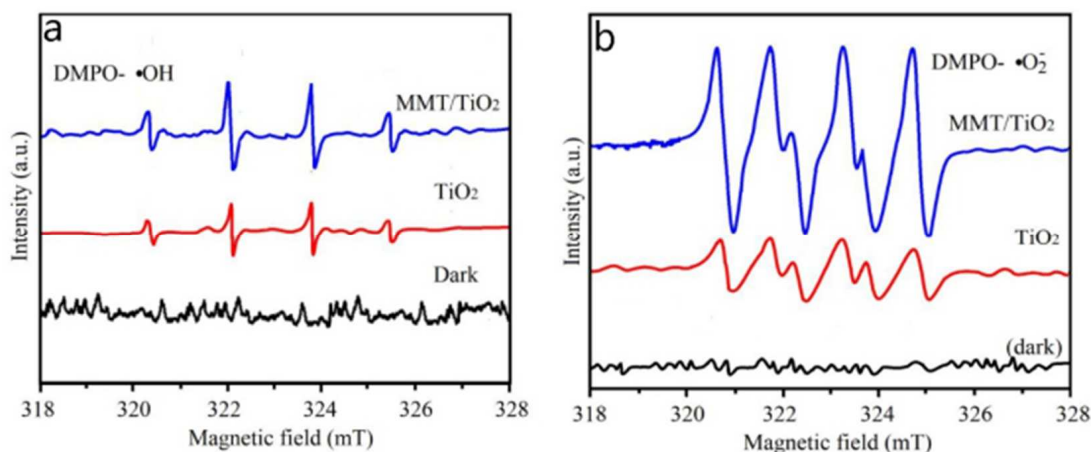


Figure 9. Electron paramagnetic resonance signals of (a) 5,5-dimethyl-pyrroline N-oxide (DMPO)- $\cdot\text{OH}$ and (b) $\text{DMPO}\cdot\text{O}_2^-$ obtained for catalysts irradiated with visible light.

The EPR signal of the $\text{DMPO}\cdot\text{O}_2^-$ adduct ($g = 2.009$, intensity ratio = 1:1:1:1) was also more intense for TiO_2 -MMT composites than for pure TiO_2 (Figure 9b). This adduct was produced via the reduction of O_2 by the electrons in the conduction band of TiO_2 -MMT (-0.08 V; $\text{O}_2/\cdot\text{O}_2^-$ reduction potential = -0.046 V). Thus, the high photocatalytic activity of TiO_2 -MMT was ascribed to the enhanced production of reactive oxygen species on its surface.

Figure 10 shows the capture experiment of active substances in the process of MB degradation. In the degradation process, isopropanol (IPA), disodium ethylenediamine tetraacetate (EDTA-2Na), and p-benzoquinone (BQ) at 1 mmol were added as scavengers of hydroxyl radicals ($\cdot\text{OH}$), holes (h^+), and superoxide radicals ($\cdot\text{O}_2^-$), respectively, to further explore the role of active substances in the process of photodegradation. It was obvious that the addition of IPA, EDTA-2Na, and BQ affected the efficiency of the photodegradation of pollutants, indicating that $\cdot\text{OH}$, h^+ , and $\cdot\text{O}_2^-$ played an important role in the process of photodegradation, and the inhibitory effect of BQ was the most obvious. Therefore, $\cdot\text{O}_2^-$ played a more important role in the process of photocatalytic degradation. This was consistent with the test results of EPR. As shown in Figure 10, $\text{DMPO}\cdot\text{O}_2^-$ had more obvious peaks under light conditions. In addition, by PL analysis, the recombination rate of the electron hole was lower, and the electron and hole functioned separately for a longer time, so the sample had better photocatalytic efficiency.

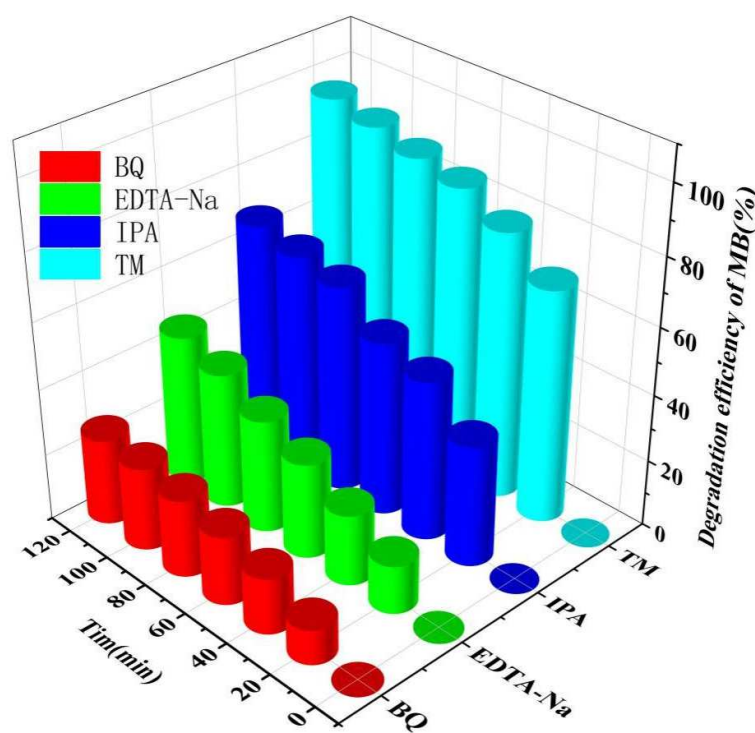


Figure 10. Trapping experiment of active substances during photocatalytic degradation of TiO₂-MMT.

2.3. N₂ Adsorption–Desorption Isotherms, Light Absorption, and Behavior of Photogenerated Charge Carriers

By testing the N₂ adsorption–desorption isotherms of TiO₂ and 30%-TM, the specific surface area of these catalysts was obtained. As shown in Figure 11a, it can be seen that TiO₂ and 30%-TM displayed characteristic Type IV isotherms, and the shape of the hysteresis loop for these isotherms was Type H3, according to the International Union of Pure and Applied Chemistry (IUPAC) classification [49]. Besides, the BET surface area of 30%-MT was 77.069 m²/g, which was a larger surface area than pure TiO₂. The pore volume and pore diameter were 0.2489 cm³/g and 15.192 nm, respectively (Figure 11a and Table 3). Furthermore, Figure 11b shows the pore diameter distribution curves, showing that the 30%-TM featured a shift in the distribution curve to larger pore sizes and the broadening of its shape. Therefore, the surface of 30%-MT can provide more active reaction sites.

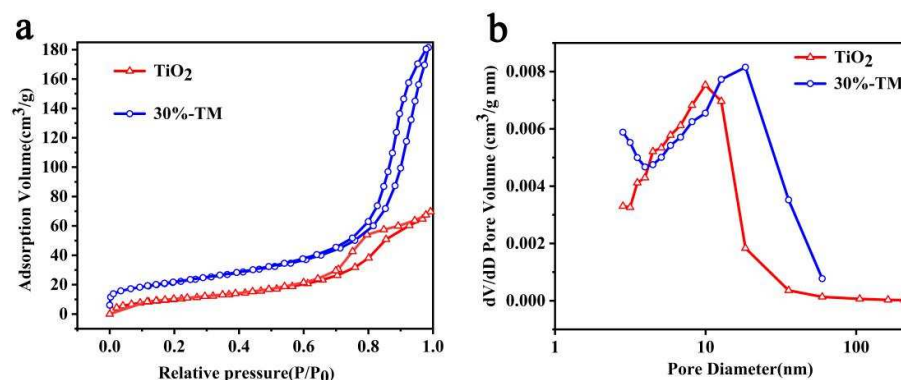


Figure 11. (a) Nitrogen adsorption–desorption isotherms of TiO₂ and 30%-TM and (b) the pore size distribution of TiO₂ and 30%-TM.

Table 3. BET parameters of TiO₂ and 30%-TM.

Sample	BET Surface Area (m ² /g)	BJH Pore Volume (cm ³ /g)	Pore Diameter (nm)
TiO ₂	38.925	0.1179	10.001
30%-MT	77.069	0.2489	15.192

Figure 12 illustrates the UV–vis absorption spectra of TiO₂-MMT composites prepared under different conditions. Anatase TiO₂ had an absorption maximum at 387 nm and an optical band gap of 3.2 eV [50]. The absorption edge of TiO₂-MMT shifted in the direction of the wavelength increase, implying a red shift [51], which can be attributed to the production of numerous empty orbitals and defects by the transition metal elements (Fe and Mn) present in MMT. Simultaneously, several studies have reported a blue shift in the absorption edge of TiO₂-MMT nanocomposites, ascribing this to the quantum confinement effects [52].

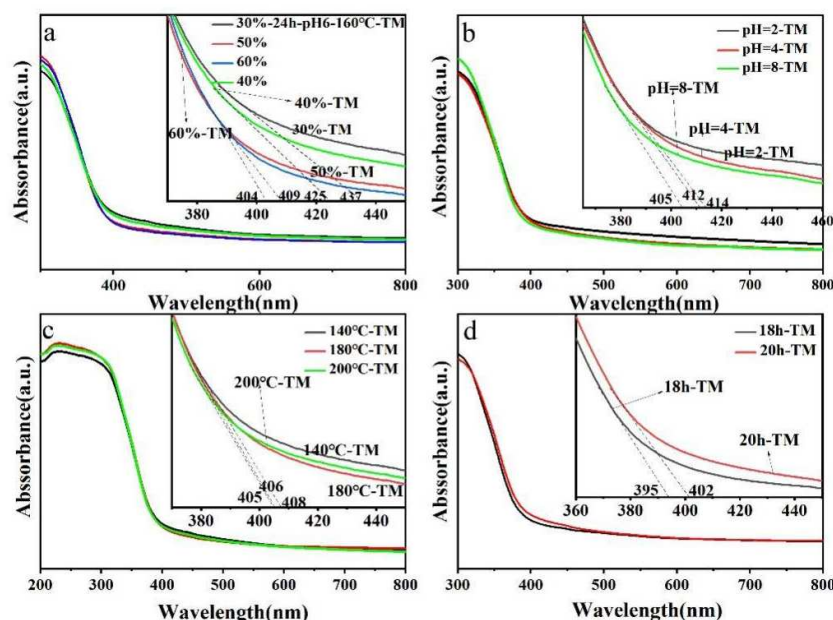


Figure 12. Ultraviolet-visible absorption spectra of TiO₂-montmorillonite (MMT) prepared using (a) different TiO₂/MMT mass ratios at a reaction temperature of 160 °C, a dwelling time of 24 h, and a pH of 6; (b) different pH levels with a reaction temperature of 160 °C, a dwelling time of 24 h, and a TiO₂ content of 30 wt%; (c) different reaction temperatures with a dwelling time of 24 h, a pH of 6, and a TiO₂ mass ratio of 30 wt%; and (d) different dwelling times at a reaction temperature of 160 °C, a pH of 6, and a TiO₂ mass ratio of 30 wt%. Inset images show expansions of the 370–450 nm region.

Figure 12a shows that the samples with a TiO₂ mass ratio of 30 and 60 wt% featured absorption edges at 437 and 404 nm, which were red-shifted by 50 and 17 nm, respectively, compared with that of anatase TiO₂ (387 nm, 3.2 eV). The corresponding red shifts for 40%-TM (425 nm) and 50%-TM (409 nm) were 38 and 22 nm, respectively. Thus, 30%-TM exhibited the largest red shift and featured the highest visible-light-absorbing ability [29], and thus, they potentially had the highest photocatalytic activity [53]. Figure 12b illustrates the effects of pH on the absorption spectra of TiO₂-MMT composites. Samples prepared at pH 2, 4, 6, and 8 exhibited red-shifted absorption edges relative to that of the anatase TiO₂ by 27, 25, 50, and 18 nm, respectively (Figure 8b). Thus, the sample prepared at pH 2 featured the best visible-light-absorbing ability.

Figure 12c shows the effect of the reaction temperature on recombination light absorption. The samples prepared at 140, 160, 180, and 200 °C have absorption edges at

408, 437, 406, and 405 nm, respectively (the respective red shifts relative to pure anatase TiO_2 equaled 21, 50, 19, and 18 nm). Figure 12d demonstrates the effect of dwelling time, revealing that samples prepared using dwelling times of 18, 20, and 24 h had absorption edges of 395 nm, 402 nm, and 437 nm, respectively. Therefore, the sample prepared using a dwelling time of 24 h had the best combination of absorption ability.

In order to further explore the optical properties of the samples, XPS was applied. Figure 13 shows the XPS peak of the pH = 2-TM and the 30%-TM nanoparticles. The Ti 2p peak was measured, as shown in Figure 13a, and the O 1s peak, Si 2p peak, and Ti 2p peak of 30%-TM were detected, as illustrated in Figure 13b–d, respectively. Most studies have pointed out that pure TiO_2 only presents the Ti $2p_{1/2}$ peak and Ti $2p_{3/2}$ peak, and these were attributed to Ti^{4+} [54]. However, for TM composites, two new peaks appeared (Figure 13a,d), corresponding to $\text{Ti}^{3+} 2p_{1/2}$ and $\text{Ti}^{3+} 2p_{3/2}$, respectively. For pH = 2-TM, two peaks appeared at 456.93 eV and 463.7 eV, and two peaks for 30%-TM appeared at 456.8 eV and 463.6 eV. From the corresponding area of each peak, the ratio of $\text{Ti}^{3+}/\text{Ti}^{4+}$ of pH = 2-TM and 30%-TM was approximately 18.83% and 20.81%, respectively. Obviously, 30%-TM had the highest Ti^{3+} content, and the minimum band gap of 30 TM was 2.76 eV (Figure 14), which meant that it had better light absorption capacity and better photocatalytic performance.

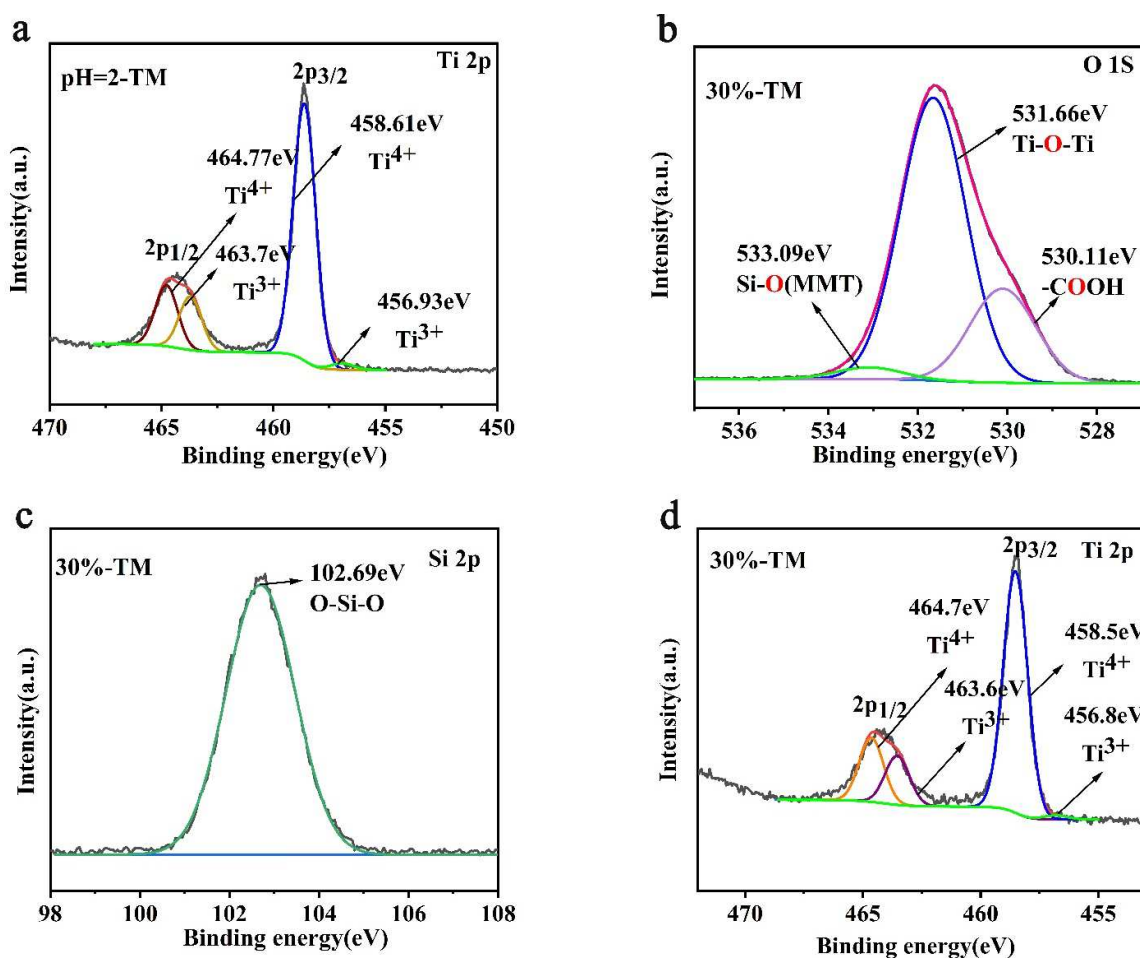


Figure 13. (a) XPS spectra (Ti 2p) of pH = 2-TM, and XPS spectra of 30%-TM. (b) O 1s; (c) Si 2p; (d) Ti 2p spectra.

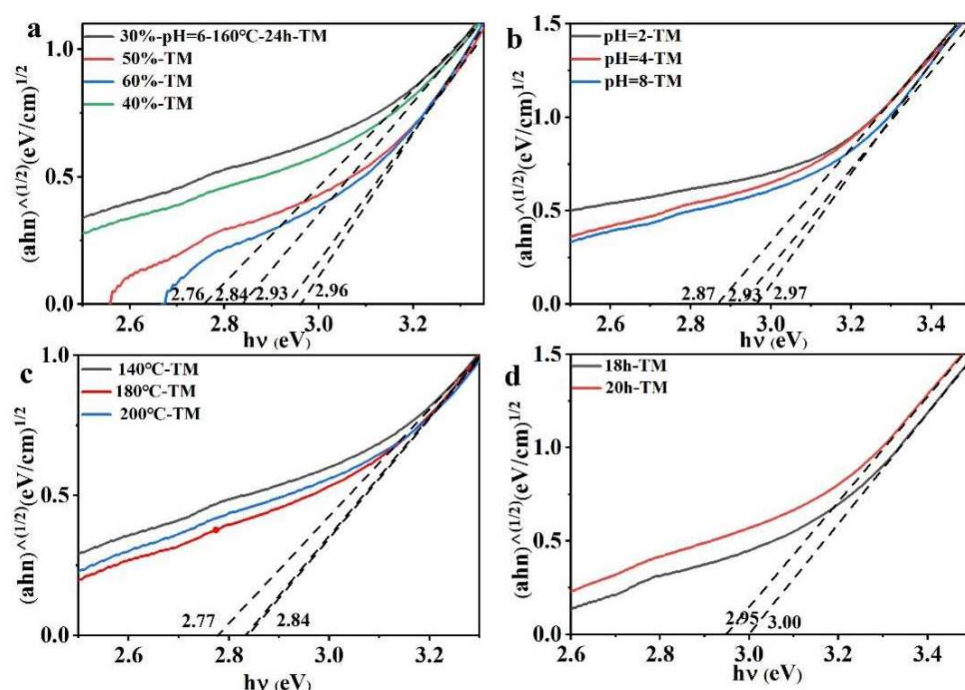


Figure 14. Tauc plots of TiO₂-montmorillonite (MMT) composites prepared using (a) different TiO₂/MMT mass ratios at a reaction temperature of 160 °C, a dwelling time of 24 h, and a pH of 6; (b) different pH values at a reaction temperature of 160 °C, a dwelling time of 24 h, and a TiO₂ mass ratio of 30 wt%; (c) different reaction temperatures with a dwelling time of 24 h, a pH of 6, and a TiO₂ content of 30 wt%; and (d) different dwelling times at a reaction temperature of 160 °C, a pH of 6, and a TiO₂ mass ratio of 30 wt%.

As presented in Figure 13b, the photoelectron peaks for O 1s were observed at 530.11, 531.66, and 533.09 eV, provided by carboxyl group, TiO₂, and MMT, respectively [19]. Carboxyl can increase the hydrophilicity of materials in the process of photocatalysis. The peak at 102.69 eV in Si 2p can be ascribed to MMT.

Figure 15a shows the EIS of TiO₂, 30%-TM and pH = 2-TM, and the PL intensity of TiO₂, 30%-TM, 50%-TM, pH = 2-TM and 18 h-TM. In the EIS results, 30%-TM had the smallest radius and had higher charge transfer efficiency, while TiO₂ had the highest radius and the smallest charge transfer efficiency. Figure 15b presents the photocurrent versus time (I-t) curve of the prepared samples with off and on rotations of visible light irradiation. The photocurrent intensity of 30%-TM was obviously higher than that of TiO₂. This point was also verified by the PL analysis. Figure 15c shows the PL intensity of TiO₂, 30%-TM, 50%-TM, pH = 2-TM, and 18 h-TM. The intensity of the PL peak indicated the recombination rate of photogenerated electrons and holes under light irradiation. Therefore, 30%-TM had better charge transfer ability, and a lower recombination rate of photogenerated electrons and holes than the samples prepared under other conditions.

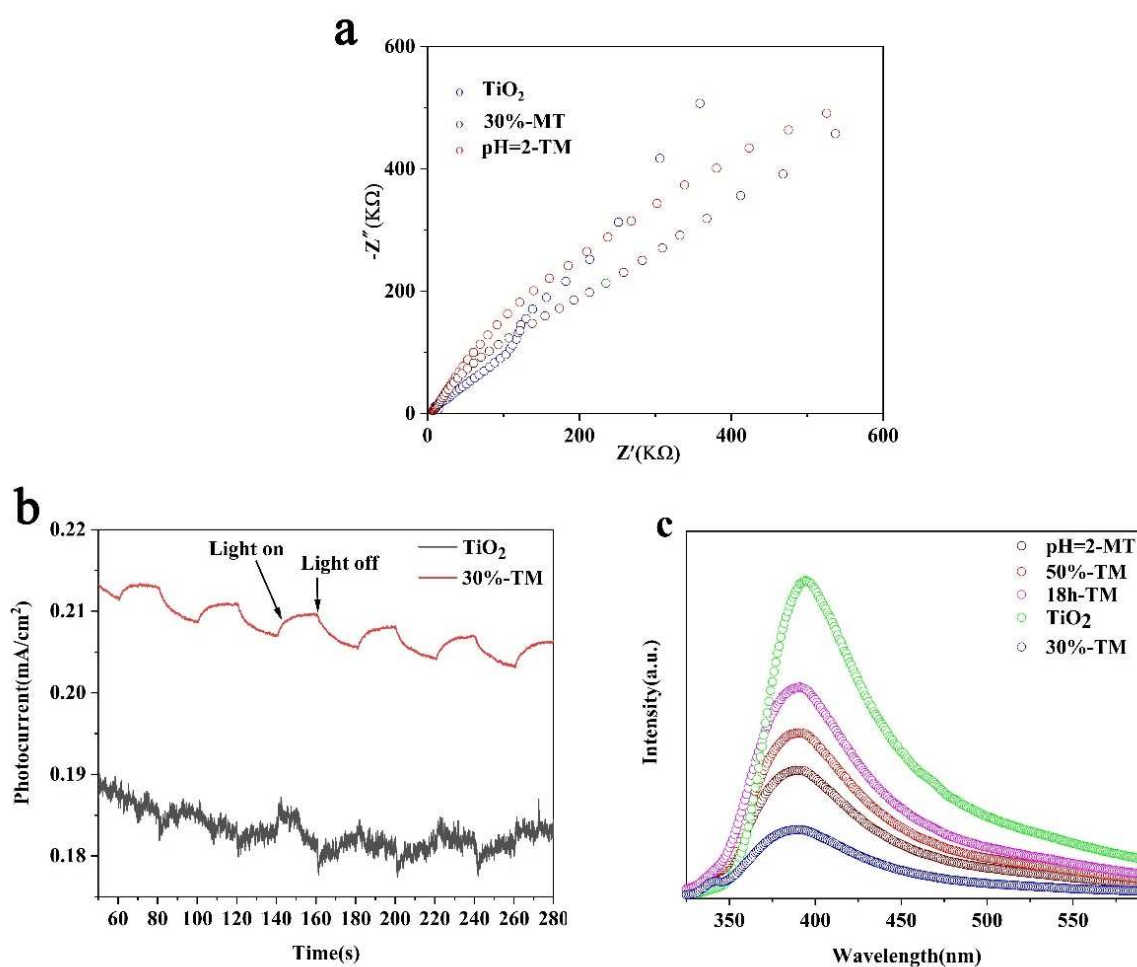


Figure 15. (a) EIS Nyquist plots of TiO_2 , 30%-MT, and pH = 2-TM. (b) Transient photocurrent responses of TiO_2 and 30%-MT. (c) Analysis of PL of TiO_2 , 30%-MT, pH = 2-TM, 50%-TM, and 18 h-TM.

2.4. Mechanism of Photocatalytic

Figure 16 illustrates a plausible mechanism of MB photodegradation by the investigated catalysts. For a better representation of the direct charge transfer in the composite, we estimated the positions of the conduction band (CB) and the valence band (VB) as follows:

$$E_{\text{VB}} = \chi - E_e + 0.5E_g, \quad (1)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_g, \quad (2)$$

where χ , E_e , E_g , E_{VB} , and E_{CB} are the absolute electronegativity of TiO_2 (5.8 eV), the energy of electrons at the standard hydrogen electrode (4.8 eV), the band gap of 30%-TM, the VB boundary of 30%-TM, and the CB boundary of 30%-TM, respectively [55]. The values of E_{CB} and E_{VB} obtained using Equations (1) and (2) were 0.08 and 2.68 eV vs. NHE, respectively.

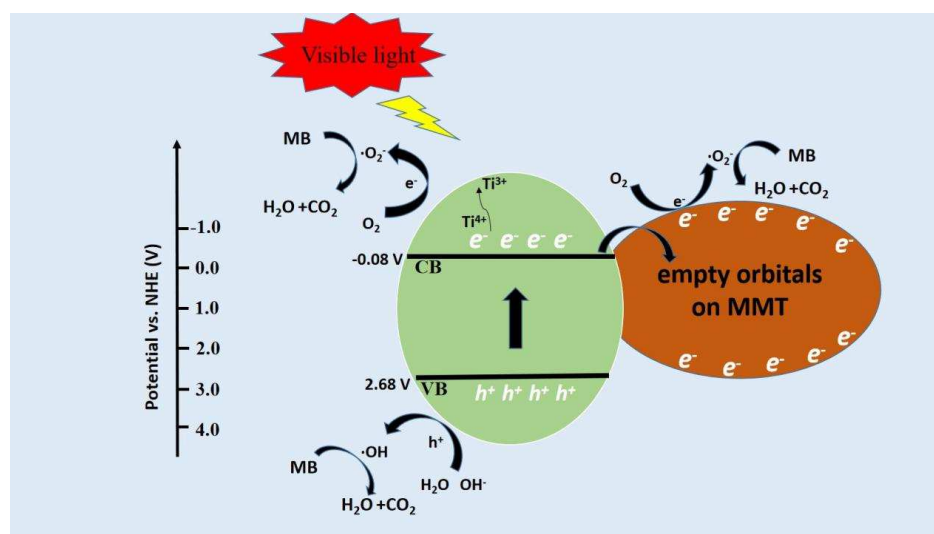
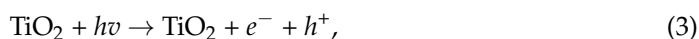


Figure 16. Suggested mechanism of methylene blue (MB) photodegradation by 30%-TM.

Compared with TiO₂, the number of oxygen vacancies in the composites increased markedly, indicating that it was easier to generate oxygen vacancies on the MMT's surface supported by TiO₂. These changes could be attributed to the combination of the Si–O bond (in the Si–O tetrahedron on the MMT's surface) and the TiO₂ hydrosol that formed the Si–O–Ti bond [19,54]. Cheng et al. reported that oxygen vacancies and Ti³⁺ content affected the band gap of TiO₂ matrix composites [19,54,56,57]. Thus, the changes in the band gap of TiO₂ matrix composites is mainly related to the number of oxygen vacancies and the content of Ti³⁺ in the material. In TiO₂-MMT composites, TiO₂ acts as a photocatalyst, producing electrons (e⁻) and holes (h⁺) under illumination. The electrons pass through the band gap and then enter the CB, leaving holes in the VB [58]. Compared with pure TiO₂, composites with MMT featured lower band gaps, thus favoring the injection of electrons into the CB. In the composite of TiO₂ and MMT, the electrons in the CB react with Ti⁴⁺ to form Ti³⁺, which is considered the most reactive site in the oxidation process because it can produce more oxygen vacancies to facilitate the adsorption of O₂ on the TiO₂'s surface [59]. The adsorbed O₂ molecules then react with electrons to produce highly reactive ·O₂⁻ species. Simultaneously, several electrons occupy the empty d-orbitals of metal ions in the MMT's structure [28], which indirectly delays the electron–hole recombination and then reacts with O₂ to produce ·O₂⁻ [60]. The holes react with water or adsorbed hydroxyl ions to form hydroxyl radicals (·OH). Both ·O₂⁻ and ·OH are strong oxidants that can destroy organic molecules [61] on and near the TiO₂' surface. Thus, the photocatalysis mechanism can be represented by the following equations:



The study of the structure, morphology, and chemical bonds proved that the layered structure of montmorillonite was still intact and that Si–O–Ti was successfully formed. Tao et pointed out in their research that Si–O–Ti could increase Ti³⁺ content and oxygen

vacancies in the composites [19]. In this work, the $\text{Ti}^{3+}/\text{Ti}^{4+}$ content was determined and simulated, and it increased by 20.81%. In addition, the optical absorption, electron and hole recombination efficiency, photogenerated carrier behavior, and specific surface area proved that 30%-TM had strong optical absorption capacity, low electron–hole recombination efficiency, a large specific surface area, and high Ti^{3+} content. This work also explored the role of active substances in the degradation process, which fully proved the significant role of $\cdot\text{OH}$, h^+ and $\cdot\text{O}_2^-$, and especially the degradation efficiency of $\cdot\text{OH}$. In a recent study, Thi et al. studied the efficiency and mechanism of photocatalytic degradation of MMT/ TiO_2 nanotubes [28]. Ami's group prepared a titanium dioxide composite clay photocatalyst by a microwave hydrothermal (5 min) and calcination method, which proved that a TiO_2 /bentonite photocatalyst has high photocatalytic efficiency [62]. However, in most research, only a single set of preparation conditions were explored, without the exploration of different preparation conditions. This study will play a guiding role in the compounding of clay and titanium dioxide.

3. Materials and Methods

3.1. Materials

All reagents were of analytical grade and used in accordance with the prescribed requirements. MB (>98.5%), MMT (>98%), tetrabutyl titanate (>98%), and cetyltrimethylammonium bromide (CTAB) (>98%) were purchased from Tianjin Komeo Chemical Reagent Co. Ltd., Tianjin, China. Anhydrous ethanol was purchased from Tianjin Hengxing Chemical Reagent Manufacturing Co. Ltd., Tianjin, China.

3.2. Preparation of TiO_2

Tetrabutyl titanate (2.3 mL) and deionized water (30 mL) were mixed and stirred for 30 min to achieve complete homogenization. The homogeneous solution was then transferred to a 100 mL polytetrafluoroethylene-lined stainless steel reactor and heated at 160 °C for 24 h. After washing, the samples were placed on an evaporation dish and oven-dried at 80 °C for 12 h to obtain TiO_2 .

3.3. Preparation of TiO_2 -MMT Composites

TiO_2 -MMT composites with TiO_2 mass ratio of 30, 40, 50, 60, and 70 wt% were prepared at different reaction pH values (2, 4, 6, and 8), reaction temperatures (140, 160, 180, and 200 °C), and dwelling times (18, 20, and 24 h) (Figure 17).

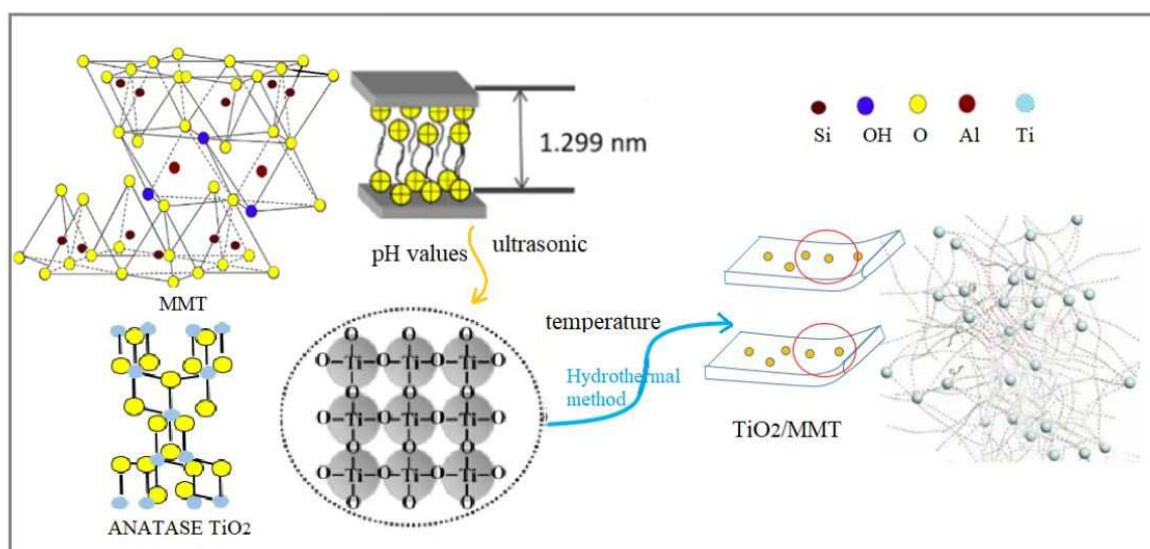


Figure 17. Schematic synthesis of TiO_2 -montmorillonite (MMT) composites.

Tetrabutyl titanate (1.7, 2.3, 2.8, 3.3, or 3.9 mL) and deionized water (30 mL) were mixed and stirred for 15 min to ensure uniform dispersion. Separately, MMT (1.0 g) was mixed with deionized water (80 mL) in a beaker, which was sealed with clingfilm to prevent evaporation; the suspension was stirred for 4 h. The solution's pH was adjusted to 2, 4, 6, or 8. The solution was allowed to stand for 5 min to ensure homogeneity and transferred to a 100 mL polytetrafluoroethylene-lined stainless steel reactor. The mixture was heated at 140, 160, 180, or 200 °C for 18, 20, or 24 h, and subsequently cooled to room temperature. After washing, the samples were placed on an evaporation dish and oven-dried at 80 °C for 12 h to obtain TiO₂-MMT composites; these composites were denoted as w%-pH = x - y °C-zh-TiO₂-MMT, where w, x, y, and z are the TiO₂ loading, pH, reaction temperature, and dwelling time, respectively.

3.4. Characterization

The phase composition was probed by X-ray diffraction (XRD; Bruker D8 ADVANCE) in the 2 θ range of 5–90°. The morphology and composition were observed by scanning electron microscopy (SEM; FEI INSPECT F50) coupled with energy-dispersive X-ray spectroscopy. Optical absorption was analyzed by ultraviolet–visible spectroscopy (UV-vis; JASCO V-600). Infrared absorption was analyzed by Fourier transform infrared spectroscopy (FTIR; IR Prestige-21) within the range of 400–4000 cm^{−1}. The surface Ti (Si or O) states of the samples were obtained by X-ray photoelectron spectrometry (XPS, Thermo SCIENTIFIC ESCALAB 250Xi). The photoluminescence (PL) spectra for solid samples were obtained using a Shimadzu RF6000 spectrophotometer with excitation wavelength of 305 nm. The surface area of the samples was obtained by applying the Brunner–Emmett–Teller (BET, BELSORP MaxII) method to the N₂ adsorption–desorption isotherms.

All electrochemical measurements were carried out in an electrochemical workstation (RST5210F, Shanghai Shiruisi instrument Technology Co., Ltd., Shanghai, China.). The electrochemical impedance spectroscopy (EIS) was conducted using an electrochemical workstation under visible light and a forward bias of 0.5 mV at the frequency range from 1 Hz to 200 Hz. Photocurrent intensity was measured in an electrolyte of 50 mL 0.2 mol/L Na₂SO₄, 30%-TM, and TiO₂ as described above. A xenon lamp equipped with a 420 nm cutoff filter was the light source, and the switching cycle was 20 s.

3.5. Photocatalytic Performance Evaluation

The ability of photocatalysts to (i) adsorb and (ii) photodegrade organic pollutants in wastewater was probed in the dark and under irradiation with visible light, respectively, using MB as a model at room temperature.

The aqueous solution of MB was mixed with the catalyst of choice (0.03 g). In the dark, the mixture was stirred for 30 min for (i), while it was irradiated with a xenon lamp (CEL-PF300-T8) at a power density of 100 mW/cm² for (ii). Subsequently, 5 mL aliquots of the dispersion were sampled every 20 min and centrifuged at 7000 rpm for 5 min. Finally, to determine the MB removal efficiency, the absorbance of the supernatant was measured; for (ii), the absorbance was measured in the range of 400–800 nm.

4. Conclusions

TiO₂-MMT composites with different TiO₂ contents were hydrothermally prepared at different pH values, reaction temperatures, and dwelling times, and evaluated as photocatalysts for MB degradation. Instrumental analysis revealed that the best-performing composite (30%-TM; TiO₂ content = 30 wt%) had the smallest band gap of 2.76 eV, a unit cell volume of 92.43 Å³, a crystallite size of 9.28 nm, and a relatively uniform distribution of TiO₂ particles on the MMT's surface. The absorption threshold of 30%-TM was red-shifted by 50 nm compared with that of anatase TiO₂ (387 nm, band gap = 3.2 eV), which enhanced the visible-light absorption and visible-light-induced activity. The intensity of the PL peak, EIS, and photocurrent indicated that 30%-TM had better charge transfer ability and a lower recombination rate of photogenerated electrons and holes than the samples prepared under

other conditions. After irradiation for 2 h with visible light, 30%-TM achieved an MB removal efficiency of 95.6%. Therefore, the compounding and modification of clay materials in this study provides a train of thought for design and research.

Author Contributions: Study design and literature search, Y.Z. and B.M.; investigation and data collection, Z.B., Y.Z., B.M. and Q.C.; artwork and figures, Y.C.; software, Y.Z.; validation, Z.B., Y.Z., B.M. and Q.C.; writing—original draft preparation, B.D.; writing—review and editing, Z.B., Y.Z. and B.M.; data curation, Y.Z. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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

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