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Preparation of a Novel Nanostructured Lead Titanate Composite Photocatalyst and Its Degradation of Organic Dyes under Visible Light

Yu-Hsun Nien ^{*}, Yan-Liang Lin, Zih-Jie Syu, Ming-Sheng Liu and Ting-Yu Huang

Department of Chemical and Materials Engineering, National Yunlin University of Science and Technology,
123 University Road, Section 3, Douliou 64002, Taiwan

* Correspondence: nienyh@yuntech.edu.tw

Abstract: Photocatalytic dye degradation is an energy-saving, environmentally friendly and sustainable way of managing potentially toxic wastewater from the textile industry. PbTiO_3 was prepared using a solid-state reaction method, and an optimal ratio of $\text{PbTiO}_3/\text{TiO}_2/\text{g-C}_3\text{N}_4$ photocatalyst was synthesized using the sol-gel method to test its ability to decompose organic dyes. Methylene blue (MB) was selected as a target dye to test the photocatalytic effects. SEM results showed that the synthesis of a $\text{PbTiO}_3/\text{TiO}_2/\text{g-C}_3\text{N}_4$ photocatalyst yielded a unique nano structure with many surface pores. UV-Vis analysis demonstrated that the novel composite photocatalyst had higher visible light absorption, and a reduced energy gap. Experimental results showed that of the samples tested, PTO/TO/CN 1.0 showed the best photocatalytic effect on the removal of MB. Under visible light, the removal rate of MB by PTO/TO/CN 1.0 was up to 98.79%. The novel PTO/TO/CN 1.0 photocatalyst exhibited relatively high MB adsorption and had a high photocatalytic ability.

Keywords: photocatalytic; lead titanate (PbTiO_3); titanium dioxide (TiO_2); graphitic carbon nitride ($\text{g-C}_3\text{N}_4$)



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1. Introduction

Rapid global growth and industrialization have drawn attention to issues associated with supporting an increasing population, such as water pollution. Water quality and availability have a significant impact on human health, but certain areas of human development are detrimental to the supply of potable drinking water, including synthetic dyes from the textile industry, used in printing and dyeing and leather and paint manufacturing. All of these industries continue to grow in size and scope, but the textile industry stands out as a major consumer of water and producer of colored wastewater, leading to significant water pollution [1–3]. In addition to this, the government response to recent global health events led to a massive increase in the demand for printed surgical masks, leading to even greater levels of water pollution [4].

Currently, the environmental risks associated with industrial wastewater discharge remain a highly pressing concern. Consequently, there is a global push to actively promote awareness of the recycling, purification, and reuse of industrial wastewater. Numerous types of dyes have been used for coloring products, but to meet color requirements, highly water-soluble and reactive organic dyes are used which leads to approximately 10–20% of the dye being washed out in the final product cleaning stages. This byproduct is not consumable by humans, is harmful to ecosystems, and in some cases is carcinogenic or mutagenic [4,5].

Approximately 80% of the dye wastewater generated by the textile industry dyeing process is discharged into the environment with no pretreatment. The impact from dye runoff is not only direct, but also absorbed by animals and plants, potentially causing indirect harm to human health. Methylene blue (MB) is a commonly used basic dye in cotton fabric

production, and it is known to be harmful to the human body [6,7]. Various methods have been employed to remove MB from factory wastewater, but so far photocatalytic oxidation is the most cost-effective. This approach utilizes light absorption via a photocatalyst to initiate a photocatalytic reaction to induce dye degradation, which reduces the need to expend additional energy [8].

A photocatalyst is a catalyst capable of absorbing light energy and converting it into chemical energy to enable a catalytic reaction. When a photocatalyst absorbs light from the sun, or any other light source, electrons in the valence band absorb the light energy and transition to the conduction band. This transition results in the creation of electron-hole pairs because electrons tend to move to the surface of the photocatalyst while leaving behind holes in their original positions [9,10]. The separated electron-hole pairs can then subsequently migrate to the surface of the photocatalyst. On the surface, these separated electrons and holes undergo a redox reaction, and when adsorbed onto pollutants they initiate a degradation process, removing the pollutant [11].

Lead titanate (PbTiO_3) perovskites possess several notable properties, including piezoelectricity, ferroelectricity, and giant magnetoresistance. As a material, they can be easily prepared using a simple and rapid solid-mixing method, and many researchers adopt this approach when exploring various PbTiO_3 applications. PbTiO_3 is commonly utilized as a P-type semiconductor in solar cells, but other transition metal oxides with Pb^{2+} ions also have the ability to absorb visible light due to their small energy gap and high conductivity, making them ideal for use in solar cells [6,12,13]. Due to these properties, PbTiO_3 is also well-suited for use as a tool to degrade organic pollutants via light catalysis [14–16]. For example, Shulan Wang et al. [17] have incorporated $\text{g-C}_3\text{N}_4$ into PbTiO_3 using a hydrothermal method, and $\text{g-C}_3\text{N}_4$ can build a heterostructure and achieve effective charge separation, thereby enhancing the photocatalytic activity. However, the photocatalytic activity of PbTiO_3 is hindered by mismatches in material functions [18,19].

Titanium dioxide (TiO_2) nanomaterials can be applied in a variety of industrial fields, such as catalysis, separation, sensors, paints, and dye-sensitized solar cells (DSSCs) [20,21]. TiO_2 exists in three crystal forms: anatase, rutile, and brookite. Among these, the anatase variety exhibits a small energy gap of 3.2 eV, and has a smaller grain size which can enhance dye loading [22,23]. The selective epitaxial growth of overlapping TiO_2 on the cathode is a technique that reduces (or in some cases eliminates) the barrier of PbTiO_3 , decreasing the energy gap of the photocatalyst and enhancing visible light absorption [24].

Graphitized carbonitrides are synthesized through the polyaddition and polycondensation of precursors containing carbon and nitrogen atoms. $\text{g-C}_3\text{N}_4$ can be prepared easily via thermal polymerization. Initially, urea forms a melamine structure, and this structure then undergoes polymerization to create a stable polymer structure as the temperature increases. At a certain temperature, polyaddition and polycondensation reactions occur, resulting in sheet-like and graphite-like carbon nitride structures [25]. Also, as documented in the literature, graphitic carbonitrides synthesized from different precursors tend to show variations in surface charge and specific surface area, which in turn can affect their ability to adsorb organic dyes [26,27]. Of the possible synthesis approaches, the graphitized carbonitride synthesized from a urea precursor demonstrates the highest specific surface area and dye adsorption capacity [28]. Furthermore, Ya-Nan Li et al. [29] have successfully prepared porous $\text{g-C}_3\text{N}_4/\text{TiO}_2$ with a multi-level heterostructure by introducing a $\text{g-C}_3\text{N}_4$ sheet-like surface structure during the synthesis of TiO_2 . It was found that the heterostructure in the sample accelerates the effective separation of photo-generated electrons and holes. This strategy presents a new approach to construct and develop novel and unusual semiconductor metal oxide structures on two-dimensional materials, exhibiting high photocatalytic activity for the degradation of organic pollutants.

P25, a commercially available photocatalyst, is primarily composed of titanium dioxide. Although widely used in the market, P25 requires ultraviolet light irradiation to demonstrate its best photocatalytic result. For this reason, it is impractical for most indoor applications. To further reduce this limitation, however, PbTiO_3 and $\text{g-C}_3\text{N}_4$ may be mixed

with TiO_2 to enhance the photocatalytic activity under visible light and improve adsorption efficiency. The photocatalytic activity of a PbTiO_3 and $\text{g-C}_3\text{N}_4$ mix may effectively decompose organic wastewater more effectively under visible light conditions.

2. Experimental Section

2.1. Materials

Ethanol was purchased from the Taiwan Sugar Corporation, Tainan, Taiwan. Titanium (IV) isopropoxide (TTIP, 98 wt %), sodium nitrate, and isopropyl alcohol (IPA) were obtained from Sigma-Aldrich Chemical Co., St. Louis, MO, USA. Acetic acid was bought from J.T. Baker Chemical, Phillipsburg, NJ, USA. Methylene blue (MB) was acquired from Fluka-Sigma-Aldrich, St. Louis, MO, USA. Titanium dioxide nanopowder (anatase rutile = 4:1; 21 nm, P25) was procured from UniRegion Bio-Tech, Taoyuan, Taiwan. Lead (II) oxide (PbO) extra pure was procured from Scharlau, Barcelona, Spain.

2.2. Testing Equipment

A UV-Visible Spectrophotometer (UV-Vis, V-630) was procured from JASCO Inc., Tokyo, Japan (wavelength range of 800–200 nm). The Field Emission Scanning Electron Microscope (FE-SEM, JSM-6701F) was procured from JEOL Ltd., Tokyo, Japan (Image magnification 2000, 5000, and 10,000 times). An X-ray Diffractometer (XRD, MiniFlex II) was procured from Rigaku, Tokyo, Japan (2θ range of 80° – 10°). The Fourier Transform Infrared Spectroscopy system (FT-IR, Spectrum One and Auto magic) was acquired from Perkin Elmer, Waltham, MA, USA (wavenumber range of 4000 – 450 cm^{-1}). The Specific Surface Area and Porosimetry Analyzer (BET, ASAP 2060) was obtained from Micromeritics, Norcross, GA, USA (analysis adsorptive: N_2 , equilibration interval: 10 s, pressure range of 760–10 mmHg).

2.3. Preparation of Lead Titanate Photocatalyst

To prepare the PbTiO_3 optimally, a solid-state reaction was used. Initially, 1 g of PbO powder and 1 g of TiO_2 (P25) powder were placed in a self-made ball mill. The powders were ground and mixed evenly by the collision of the balls within the ball mill. The resultant mixture was transferred to an alumina crucible. The alumina crucible containing the mixture was subjected to calcination. The heating rate during calcination was $10\text{ }^\circ\text{C}/\text{min}^{-1}$. The crucible was heated to different temperatures, specifically $700\text{ }^\circ\text{C}$, $800\text{ }^\circ\text{C}$, $900\text{ }^\circ\text{C}$, and $1000\text{ }^\circ\text{C}$, and each temperature was maintained for 2 h. The product was split into four distinct samples according to their calcined temperatures, i.e., $700\text{ }^\circ\text{C}$ PTO, $800\text{ }^\circ\text{C}$ PTO, $900\text{ }^\circ\text{C}$ PTO, and $1000\text{ }^\circ\text{C}$ PTO, respectively, where “PTO” refers to their PbTiO_3 constituent.

2.4. Preparation of Graphitic Carbon Nitride

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) was prepared via thermal polymerization. First, 5 g urea powder was placed in an alumina crucible, and the crucible was covered with a lid. To prevent the leakage of urea gas, the entire crucible was again covered with a layer of aluminum foil. The crucible containing the urea powder was subjected to a controlled heating process, whereby the temperature was gradually increased in a calciner at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ until $550\text{ }^\circ\text{C}$. Once $550\text{ }^\circ\text{C}$ was obtained, that temperature was maintained for 4 h, until complete thermal polymerization of the urea had occurred. Post thermal treatment, the crucible was cooled to room temperature, resulting in the formation of graphitic carbon nitride.

2.5. Preparation of the $\text{PbTiO}_3/\text{TiO}_2/\text{g-C}_3\text{N}_4$ Photocatalyst

The $\text{PbTiO}_3/\text{TiO}_2/\text{g-C}_3\text{N}_4$ composite photocatalyst was synthesized using the sol-gel method. The degradation experiment showed that the photodegradation effect of PTO at $1000\text{ }^\circ\text{C}$ was superior to other PTO samples. The synthesis process involved several steps; first, a clear solution was prepared by mixing 6 mL of titanium (IV) isopropoxide

and 8 mL of acetic acid. The mixture was stirred for 15 min. Subsequently, 6 mL of acetic acid was added, and the mixture was stirred for 5 h. Then, 2 g, 1 g, 0.6 g, or 0.2 g of PbTiO_3 , together with 5 mL of distilled water, was added to the solution. The resulting mixture was stirred overnight. The solvent was removed with the mixture placed in a vacuum oven at 80 °C. The remaining powder was ground and transferred into an aluminum crucible. Following this, the powder was wrapped with aluminum foil. The crucible was placed into a segmented furnace, and the temperature was raised to 450 °C at a heating rate of 10 °C/min. The calcination process was carried out for 2 h. After cooling, the composite photocatalysts were obtained and their weight ratios of PbTiO_3 to TiO_2 were recorded as 1 PTO/TO, 0.5 PTO/TO, 0.3 PTO/TO, and 0.1 PTO/TO. The weight of TiO_2 without PbTiO_3 was 2 g.

Based on drop experiments, it was determined that the optimal weight ratio of $\text{g-C}_3\text{N}_4$ doping was 0.3 PTO/TO. To prepare this composite, 6 mL of titanium (IV) isopropoxide and 8 mL of acetic acid were mixed for 15 min to obtain a clear solution. Then, 2 g, 1 g, 0.6 g, or 0.2 g of $\text{g-C}_3\text{N}_4$ was gradually added to the 6 mL of acetic acid and stirred for 5 h. Subsequently, 5 mL of distilled water and 0.6 g of PbTiO_3 were added, and the mixture was stirred overnight. The mixture was placed in a vacuum oven at 80 °C to remove the solvent. The obtained powder was poured into an aluminum crucible and wrapped in aluminum foil. The crucible was placed in a segmented furnace and heated to 450 °C at a heating rate of 10 °C/min. The composite photocatalysts were named PTO/TO/CN (2), PTO/TO/CN (1), PTO/TO/CN (0.6), and PTO/TO/CN (0.3), corresponding to different $\text{g-C}_3\text{N}_4$ weights added to the 0.3 PTO/TO composite photocatalyst.

2.6. Characterizations

2.6.1. Characterization of the Photocatalyst

Laboratory instruments were utilized to measure and identify the synthesized photocatalyst properties, according to the temperature at which they were synthesized, the differing PTO/TO weight ratios, and the PTO/TO/CN with various $\text{g-C}_3\text{N}_4$ weights. The surface topography was characterized using field emission scanning electron microscopy (FE-SEM), the crystalline structure and composition were confirmed using an X-ray diffractometer (XRD), and the d-spacing and grain size D were calculated using Bragg's law and Scherrer's formula. FT-IR identification of the sample functional groups was used to determine whether there was a new bond. UV-Vis was utilized to analyze the photocatalyst visible light absorption and calculate the energy gap. The specific surface area of the photocatalyst and nitrogen adsorption-desorption processes were analyzed using BET, to understand the adsorption capacity.

2.6.2. Dye Adsorption and Photocatalytic Degradation Experiments

In this experiment, methylene blue (MB) was used as a model dye to compare the adsorption and photocatalytic degradation of P25 (a commercially available photocatalyst), with TiO_2 , PbTiO_3 , and the photocatalysts with various ratios of PTO/TO, PTO/TO/CN. To use the photocatalyst, 0.01 g of photocatalyst powder was mixed with 10 mL of 10 ppm MB in a 20 mL sample bottle with a stirring magnet. The photocatalyst absorbed MB in the dark for 0.5 h, and then a T25 visible light tube was used to trigger photodegradation for 2.5–3 h, with readings being taken every 0.5 h. After the adsorption period in the dark, and photodegradation in visible light, the solutions were centrifuged at 7000 rpm for 7 min. Subsequently, the photocatalyst and clarified MB solutions were examined to determine any MB concentration changes in the resultant solution using UV-Vis.

3. Results and Discussion

3.1. X-ray Diffractometer (XRD)

When preparing the PbTiO_3 , the solid mixing method was used followed by chemical sintering synthesis at different temperatures. The higher the temperature, the better the combination of PbO and TiO_2 . The XRD pattern shown in Figure 1 shows that the PbTiO_3

was successfully synthesized, as the data related closely to the standard card JCPDS No.75-0438 [30]. A change in crystallization caused by temperature is also observable. In Figure 2, the peak appears narrower where the calcination temperature is higher, especially between 31.57° and 32.52° , suggesting that the PbTiO_3 crystal may be larger when the temperature is higher.

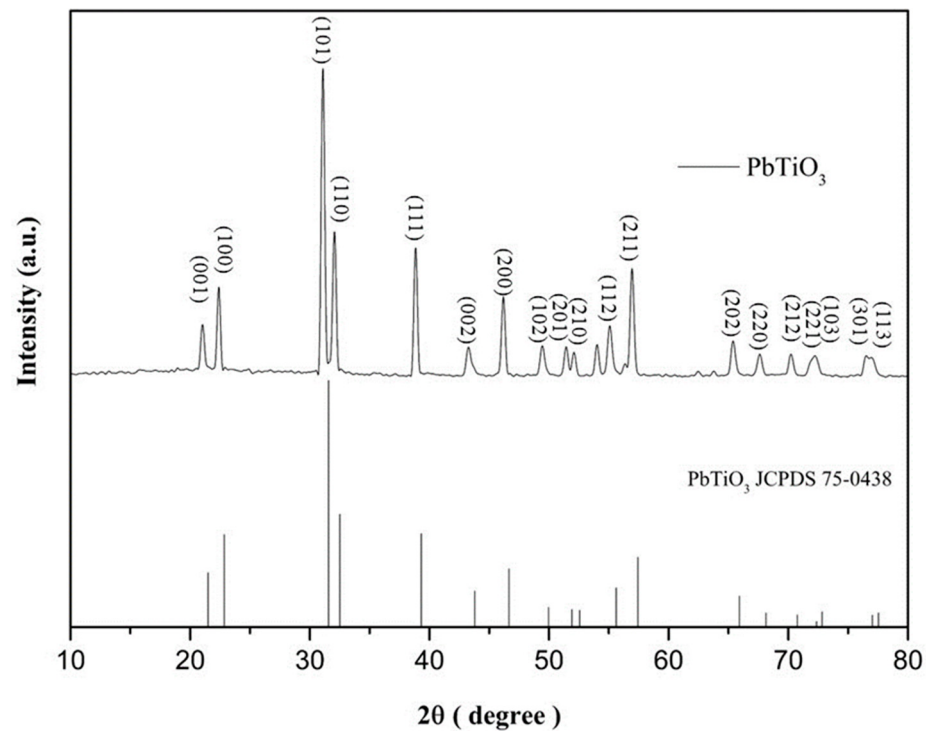


Figure 1. Comparison of XRD peaks for the 1000 °C PTO vs. JCPDS card.

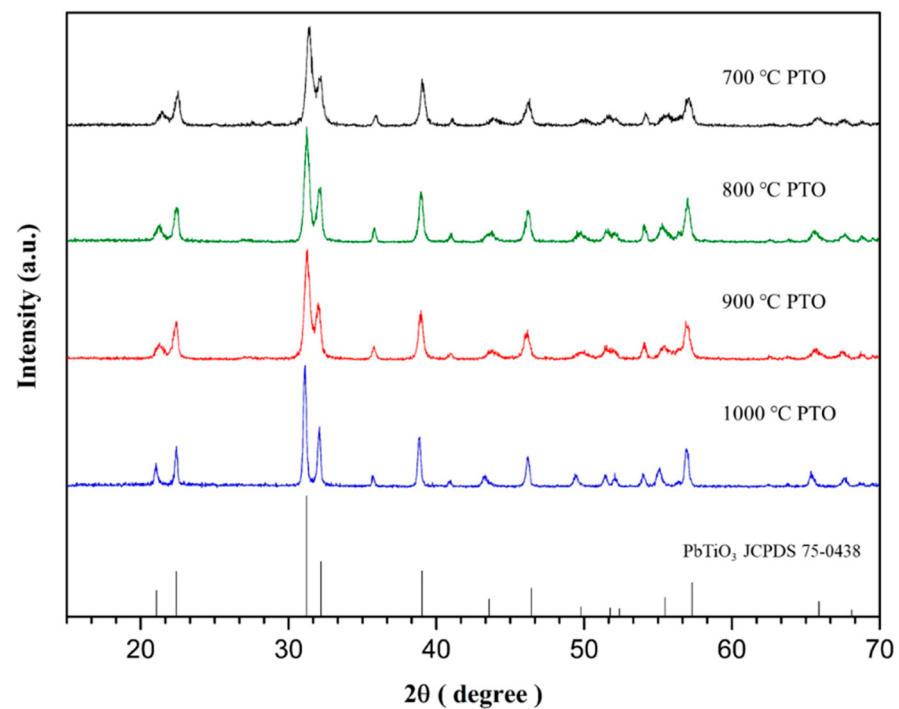


Figure 2. XRD peaks for PbTiO_3 sintered at different temperatures.

In this study, the inter-planar d-spacing of the crystal was calculated using Bragg's law, and the crystal grain size was calculated via the Scherrer equation. Bragg's law in Equation (1) and the Scherrer equation in Equation (2) were adopted from the literature. In the equations, d is the inter-planar d-spacing, θ is the diffraction angle radian, λ is the wavelength of the X-rays, ΔW is the full-width at half-maximum, and D is the size of the crystal grain.

$$2d \sin \theta = n \lambda \quad (1)$$

$$D = (0.9 \times \lambda) / (\Delta W \times \cos \theta) \quad (2)$$

The calculations were first conducted for the PbTiO_3 calcined at different temperatures, by the formula for crystals with an orientation (101). When the temperature was higher, the PbO and TiO_2 combination formed larger particles and the sintering effect was the strongest, and the particles were the largest, at 1000 °C, as shown in Table 1.

Table 1. Grain characterization of PTO synthesized at different temperatures.

	FWHM	2 θ (°)	d-Spacing (nm)	D (nm)
700 °C PTO	0.5032	31.39534	0.2847044	16.399182
800 °C PTO	0.48387	31.26207	0.285887	17.048748
900 °C PTO	0.45423	31.24562	0.2860344	18.160505
1000 °C PTO	0.3395	31.10396	0.2873047	24.289255

The XRD diffraction peak area was used to calculate the relative crystallinity (X_c) of the pure (control) sample. Generally, the total area (A_{total}) was obtained through the integration of the strongest diffraction peak being used as an indicator for the calculation made with the crystallinity, and the non-crystalline integral curve (A_m) was deducted for comparison, and the crystallinity formula was calculated as shown below. It can be seen from Table 2 that as the calcination temperature increased, the crystallinity also increased.

$$\text{Crystallinity} = (A_{\text{total}} - A_m) / A_{\text{total}} \times 100\% \quad (3)$$

Table 2. Integral area and crystallinity of PTO synthesized at different temperatures.

	Total	A_m	X_c (%)
700 °C	977.8631	339.7099	65.2600
800 °C	970.1649	313.0657	67.7307
900 °C	926.7613	197.1598	78.7259
1000 °C	864.7150	127.9308	85.2054

Several authors in the literature have already shown that the addition of PbTiO_3 to anatase TiO_2 can effectively improve the photocatalytic activity [24]. This study used the sol-gel method to prepare the anatase TiO_2 . The XRD peaks of the TiO_2 are shown in Figure 3, and the centers of the 2 θ peaks were located at 25.281°, 36.947°, 37.801°, 38.576°, 48.049°, 53.890°, 55.060°, 62.690°, and 68.762°, respectively, which corresponded to the crystal orientations of (101), (103), (004), (112), (200), (105), (211), (213), (204), and (116). Compared to the standard card JCPDS No.21-127, this indicates that the anatase TiO_2 was synthesized correctly [31].

Different weights of 1000 °C PTO were added to the TiO_2 using the sol-gel method to obtain different ratios of $\text{PbTiO}_3/\text{TiO}_2$. The XRD peaks were examined to characterize the product. Comparing the study result with the two standard cards, TiO_2 JCPDS No.21-127 and PbTiO_3 JCPDS No.75-0438, as shown in Figure 4, it can be seen that the $\text{PbTiO}_3/\text{TiO}_2$ was successfully prepared [30,31]. Because various amounts of PbTiO_3 will impact the TiO_2 grain size, it was necessary to calculate the TiO_2 grain sizes for the 2 θ peak at 25°, representing crystal orientation (101). The TiO_2 grain size of 0.3 PTO/TO was the smallest,

as shown in Table 3. We speculate that when the weight ratio of PbTiO_3 and TiO_2 is 0.3:1, PbTiO_3 may inhibit the growth of TiO_2 grains, so the D value of 0.3 PTO/TO is the smallest.

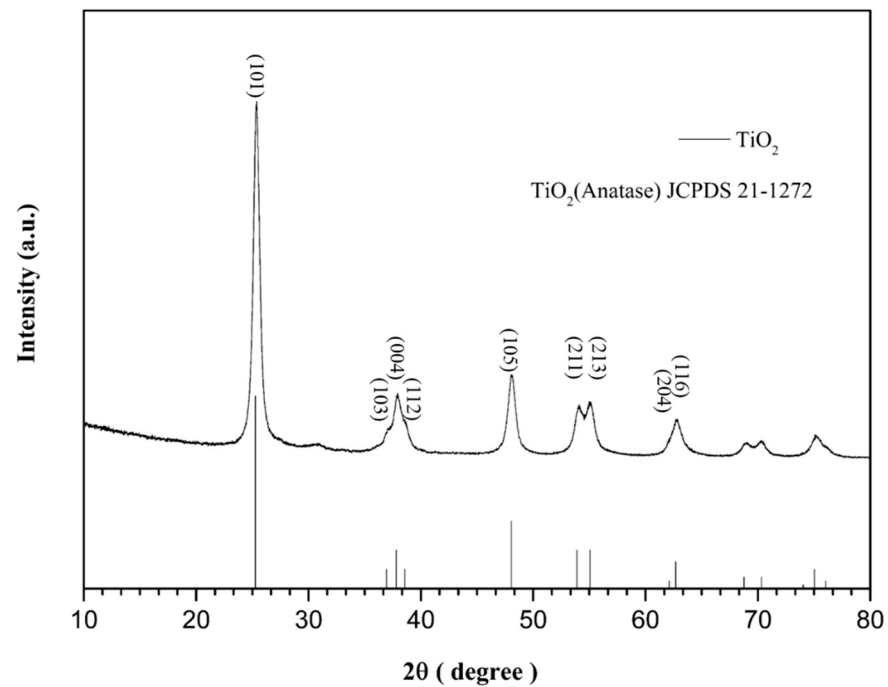


Figure 3. Comparison of XRD peaks of anatase TiO_2 vs. JCPDS card.

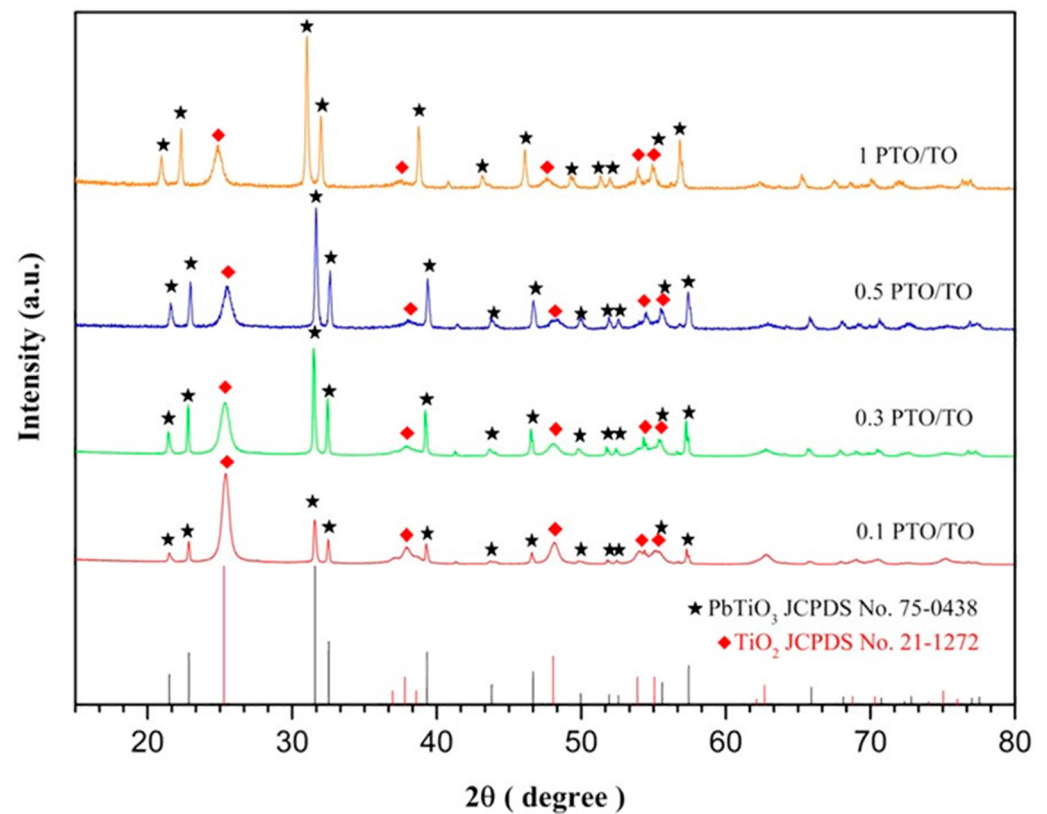
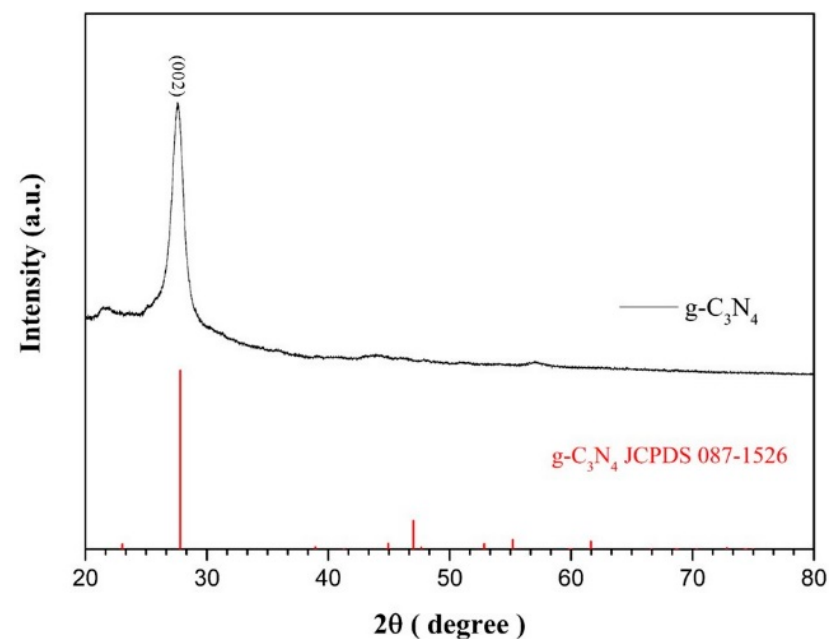


Figure 4. Comparative XRD peaks for different ratios of PTO/TO vs. JCPDS card.

Table 3. Grain characterization of PTO/TO synthesized using different weight ratios.

	FWHM	2 θ (°)	d-Spacing (nm)	D (nm)
TiO ₂	0.72578	25.37402	0.350734	11.219802
0.1 PTO/TO	0.63848	25.39777	0.350411	12.754492
0.3 PTO/TO	1.29104	25.34598	0.351115	6.3070546
0.5 PTO/TO	0.73827	25.34995	0.351061	11.029465
1 PTO/TO	0.72705	25.36456	0.350862	11.199995

g-C₃N₄ was successfully synthesized via polycondensation, as confirmed by comparing the XRD peaks with the standard card JCPDS No.98-1526, observing a characteristic peak at 26.5°, as shown in Figure 5 [32].

**Figure 5.** The comparison of XRD peaks of g-C₃N₄ vs. JCPDS card.

Different amounts of g-C₃N₄ were added to PbTiO₃/TiO₂ via the sol-gel method to synthesize a series of new PTO/TO/CN photocatalysts with different g-C₃N₄ weight ratios. Again, XRD peaks were obtained to characterize the product, and the results were compared with the standard JCPDS card, as shown in Figure 6. Adding different g-C₃N₄ weights could also affect the growth of the TiO₂ grain. As before, the grain size of TiO₂ was calculated for the 2 θ peak at 25°, representing crystal orientation (101). The more g-C₃N₄ that was added, the smaller the TiO₂ grain size was likely to be, as shown in Table 4.

Table 4. Grain characterization of PTO/TO/CN synthesized with different weight ratios.

	FWHM	2 θ (°)	d-Spacing (nm)	D (nm)
0.3 PTO/TO	1.29104	25.34598	0.351115	6.307054
PTO/TO/CN (0.3)	1.35116	25.3073	0.351643	6.025964
PTO/TO/CN (0.6)	1.09705	25.32928	0.351343	7.422080
PTO/TO/CN (1.0)	1.50451	25.31719	0.351508	5.411861
PTO/TO/CN (2.0)	2.22555	25.34864	0.351079	3.658737

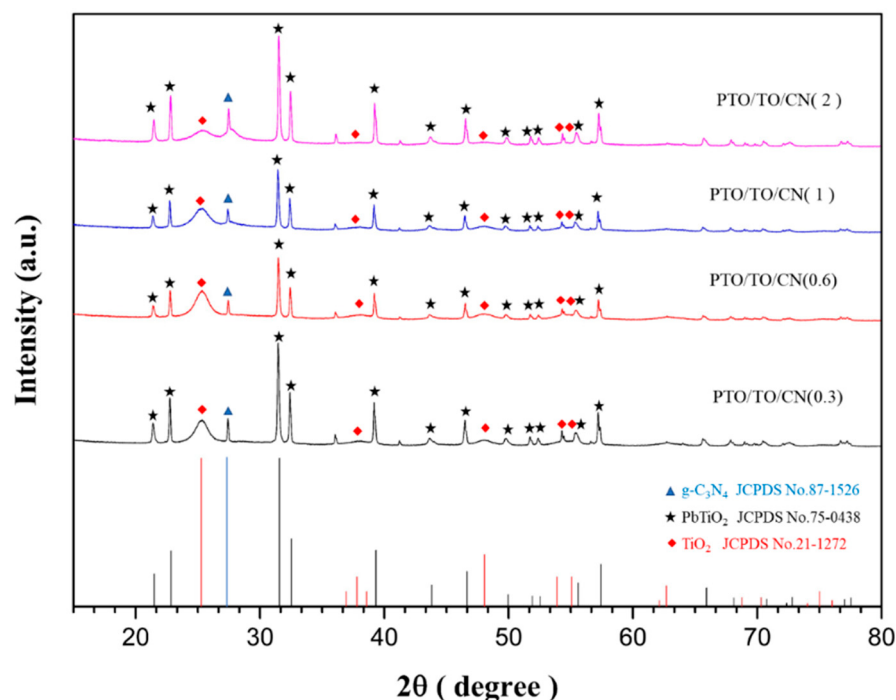


Figure 6. XRD peaks for different ratios of PTO/TO/CN vs. JCPDS card.

3.2. Field Emission Scanning Electron Microscopy (FE-SEM)

PbTiO₃ was sintered at 700 °C, 800 °C, 900 °C, or 1000 °C for 2 h. The SEM images in Figure 7 show the surfaces of the PbTiO₃ sintered samples at various temperatures under 1000× magnification. Figure 7a shows the small particles of the 700 °C PTO sample where the TiO₂ and PbTiO₃ had not completely combined and dispersed. For the higher temperature samples, as the temperature continued to increase, smaller particles began to agglomerate and combine, gradually forming spherical crystals. Figure 7d shows that the 1000 °C PTO sample was fully combined into large spherical crystals, which was consistent with the results observed in the XRD data. Figure 8a depicts the pure TiO₂ synthesized using the sol-gel method. It was found that the particles had different sizes and were dispersed. Figure 8b shows the SEM images of g-C₃N₄ under 2000× magnification, where the formation resembles stacked sheets.

Figure 9a,b represent the SEM images of PTO/TO/CN (0.3) and PTO/TO/CN (0.6), respectively, where the crystals exhibit irregular agglomeration and a rough surface. Figure 9c shows the SEM image of PTO/TO/CN (1.0), where the crystals have a unique shape resembling a pear, and the surface displays numerous indentations and protrusions, forming patterns. We speculate that the addition of g-C₃N₄ disperses PTO/TO particles on the surface of g-C₃N₄, resulting in this peculiar structure. Figure 9d depicts the SEM image of PTO/TO/CN (2.0), which also exhibits the unique structure observed in PTO/TO/CN (1.0), but most of the crystals had agglomerated into large particles.

In order to further understand the morphology of these peculiar crystals, we observed samples of PTO/TO/CN (1.0) and PTO/TO/CN (2.0) at a magnification of 5000 times, as shown in Figure 10. Figure 10a shows the unique pear-shaped crystals in PTO/TO/CN (1.0). Although there are also some large particle aggregates, the number of unique crystals is larger and the sizes are more consistent. Figure 10b shows the situation in PTO/TO/CN (2.0). Compared to PTO/TO/CN (1.0), the surface indentations and patterns of the unique crystals in PTO/TO/CN (2.0) are less pronounced and appear to be filled, resulting in a deformed and less pear-shaped morphology. Additionally, PTO/TO/CN (2.0) has fewer unique crystals, and most of them have agglomerated into large particles.

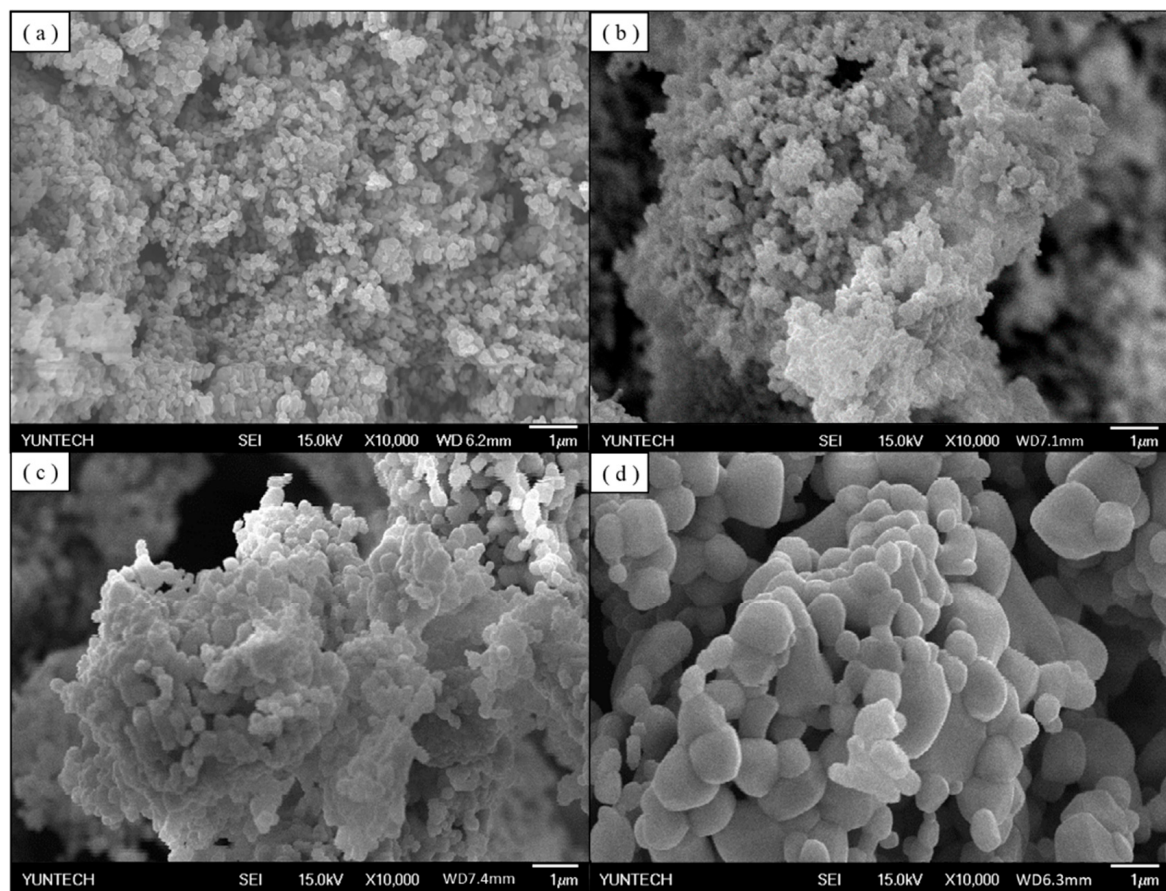


Figure 7. SEM images of (a) 700 °C PTO, (b) 800 °C PTO, (c) 900 °C PTO, and (d) 1000 °C PTO at 10,000× magnification.

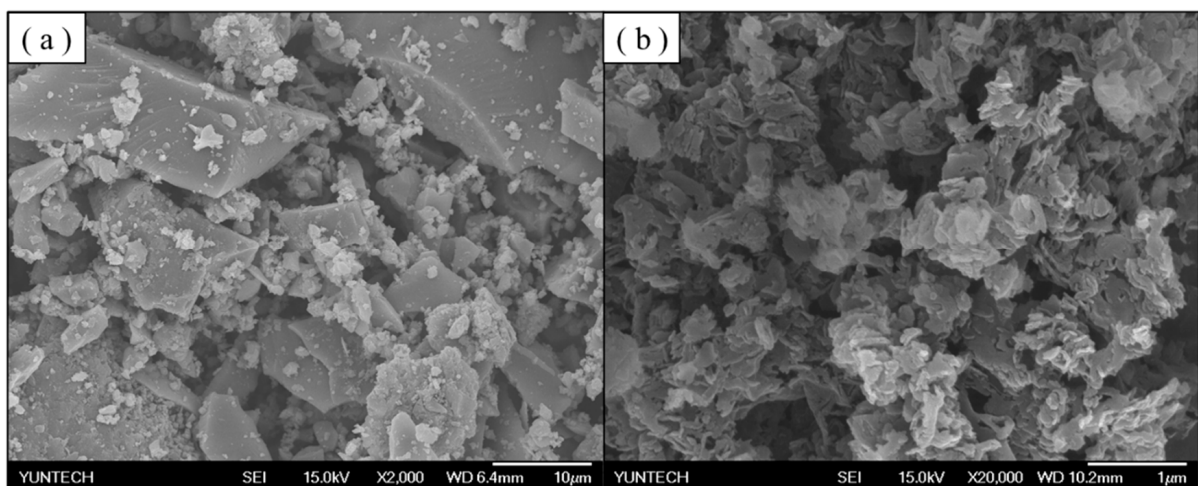


Figure 8. SEM images of (a) TiO_2 and (b) $\text{g-C}_3\text{N}_4$ at 2000× and 20,000× magnification, respectively.

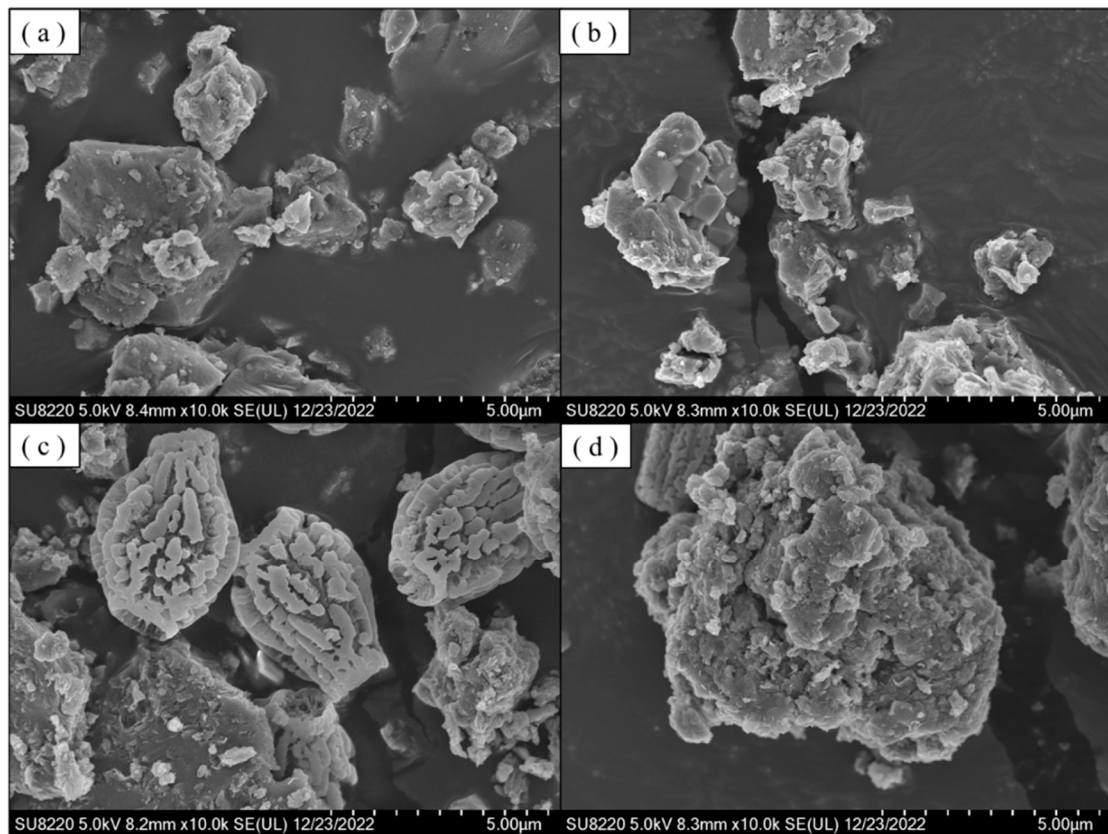


Figure 9. SEM images of (a) PTO/TO/CN (0.3), (b) PTO/TO/CN (0.6), (c) PTO/TO/CN (1), and (d) PTO/TO/CN (2) at 10,000 $\times$ magnification.

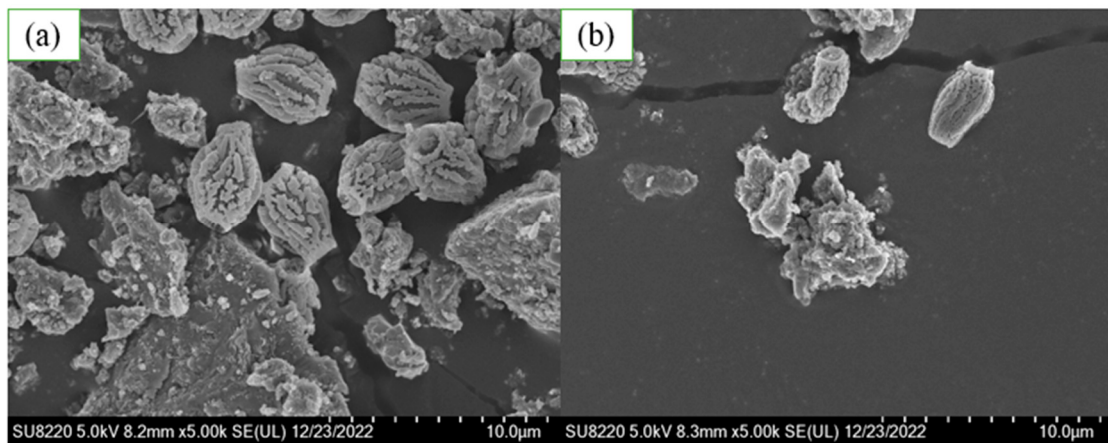


Figure 10. SEM images of (a) PTO/TO/CN (1) and (b) PTO/TO/CN (2) at 5000 $\times$ magnification.

3.3. FTIR Measurement and Analysis

Figure 11 shows the FTIR spectra of the PbTiO_3 sample. There are multiple shifts in the Ti–O–Ti stretching bands in the wavenumber range 631–570 cm^{-1} , and there is also –OH bending visible in the wavenumber range 1647–1636 cm^{-1} . The peaks corresponding to the Pb–O groups can be observed in the wavenumber range 1400–1397 cm^{-1} . The broad peak in the wavenumber range of 3457–3117 cm^{-1} indicates the absorption of the –OH stretching vibration from the H_2O molecules that adsorbed on the surface of the PbTiO_3 . Furthermore, in the 1000 $^\circ\text{C}$ sintered PTO sample, due to the formation of Pb–O–Ti bonds, a new peak formed at approximately 711 cm^{-1} . The aforesaid indicates successful chemical bonding between the TiO_2 and PbO, forming the Pb–O–Ti bond [33].

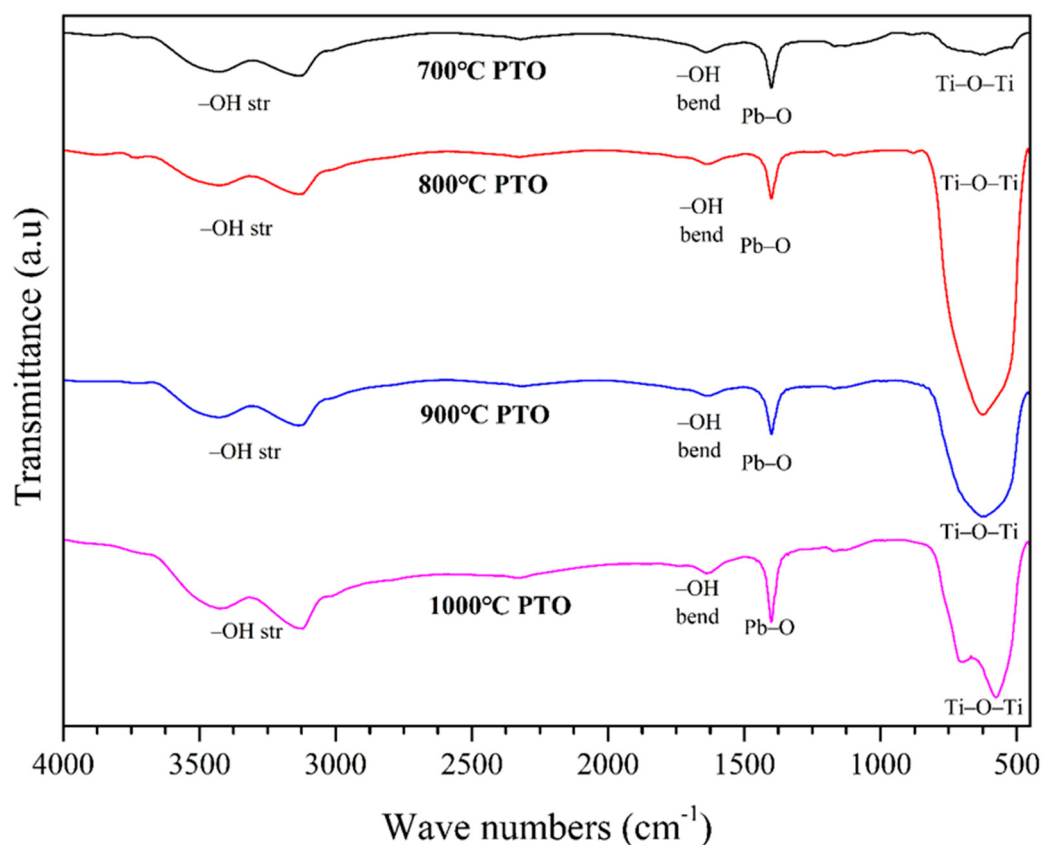


Figure 11. FTIR spectra of PbTiO_3 synthesized by sintering at different temperatures.

Figure 12 shows the FTIR spectrum of the TiO_2 , and the -OH stretching vibrations from the surface adsorbed water molecules are visible in the range $3400\text{--}3153\text{ cm}^{-1}$. The peaks at $585\text{--}523\text{ cm}^{-1}$ correspond to the Ti-O-Ti stretching vibrations, while the peak at 1630 cm^{-1} represents the Ti-O stretching and Ti-OH bending vibrations. The FTIR spectra in Figure 13 confirm the binding of the TiO_2 and PbTiO_3 in the PTO/TO composites for the $1000\text{ }^\circ\text{C}$ PTO sample and its various PTO/TO ratios. The broad peak in the range $3562\text{--}3130\text{ cm}^{-1}$ indicates -OH stretching vibrations, and absorption peaks related to the Pb-O groups were observed in the range $1400\text{--}1397\text{ cm}^{-1}$. The peaks at $585\text{--}523\text{ cm}^{-1}$ represent the Ti-O-Ti stretching vibrations, and the peaks at $720\text{--}713\text{ cm}^{-1}$ indicate the presence of Pb-O-Ti bonds. These spectra can possibly confirm the presence of both PTO and TiO_2 in the PTO/TO composites [33].

Figure 14 shows the FTIR spectra of the $\text{g-C}_3\text{N}_4$ sample, with peaks at 814 cm^{-1} (representing the bending vibration of the heterocyclic structure) and $1238\text{--}1640\text{ cm}^{-1}$ (showing the stretching vibrations of C=N or C-N bonds in the CN heterocycles). The region between 3000 and 3700 cm^{-1} represents the N-H bond stretching vibrations, and the broad peak between 3400 and 3600 cm^{-1} indicates the -OH vibrations from adsorbed water [34].

Figure 15 shows the FTIR spectra as it relates to TiO_2 , $1000\text{ }^\circ\text{C}$ PTO, $\text{g-C}_3\text{N}_4$, and different PTO/TO/CN ratios. It confirms the binding of $\text{g-C}_3\text{N}_4$ and PTO/TO in the composites. The broad peak in the range of $3562\text{--}3130\text{ cm}^{-1}$ shows the -OH stretching vibrations, and all the observed spectra exhibit an absorption band in the range $550\text{--}800\text{ cm}^{-1}$, relating to the presence of TiO_2 in all the PTO/TO/CN composites. The raised broad peak in the range $720\text{--}713\text{ cm}^{-1}$ indicates Pb-O-Ti bond absorption. The FTIR spectra relating to $\text{g-C}_3\text{N}_4$ are present in the fingerprint region $1200\text{--}1640\text{ cm}^{-1}$, confirming its presence in all PTO/TO/CN composites. The intensity of the peak at 814 cm^{-1} corresponds to the heterocyclic structure, and increases with higher amounts of $\text{g-C}_3\text{N}_4$ doping. Therefore,

based on the observed spectra, it can be inferred that the PTO/TO/CN composites contain TiO_2 , PTO, and $\text{g-C}_3\text{N}_4$.

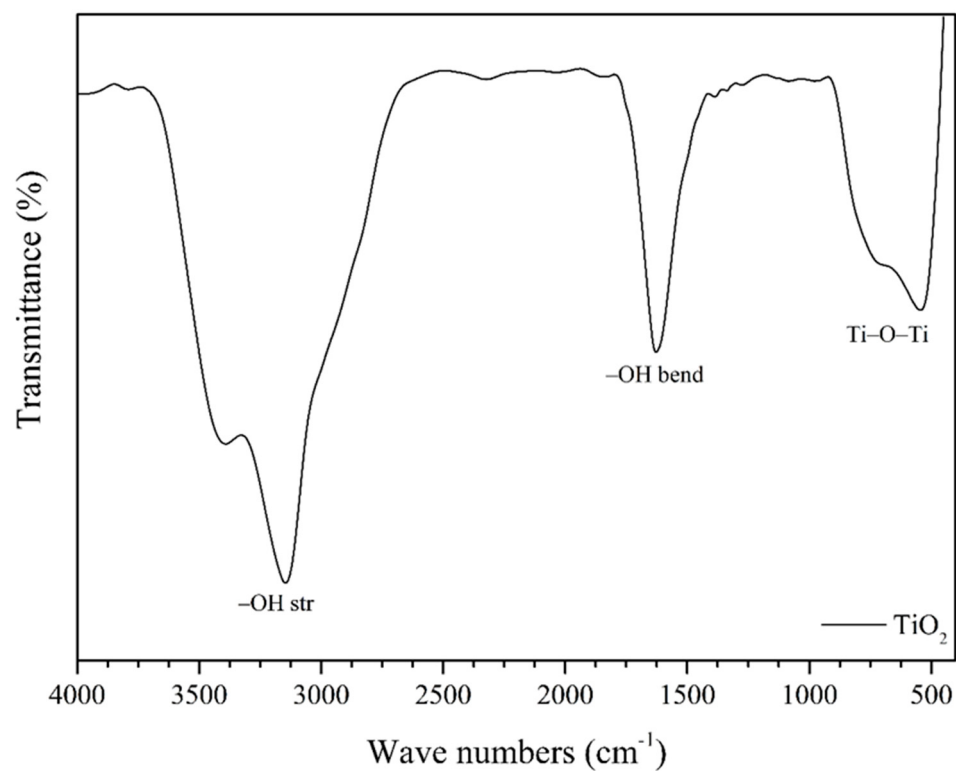


Figure 12. TiO_2 FTIR spectra.

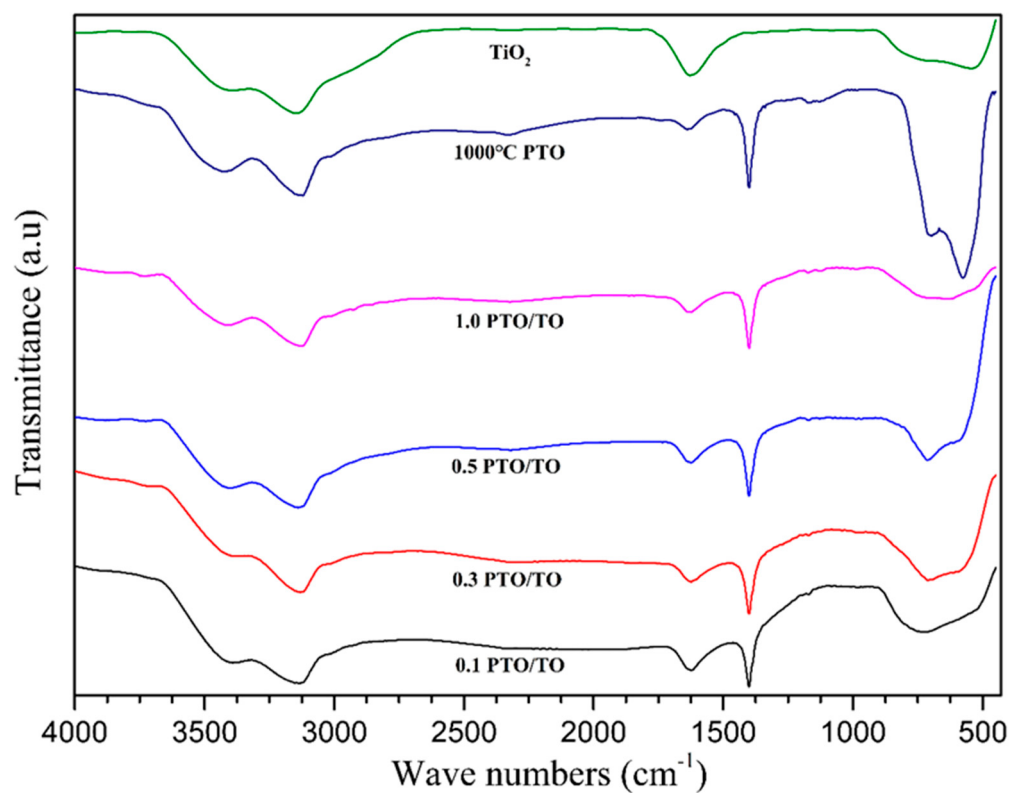


Figure 13. FTIR spectra of TiO_2 , 1000 $^{\circ}\text{C}$ PTO, and PTO/TO in various ratios.

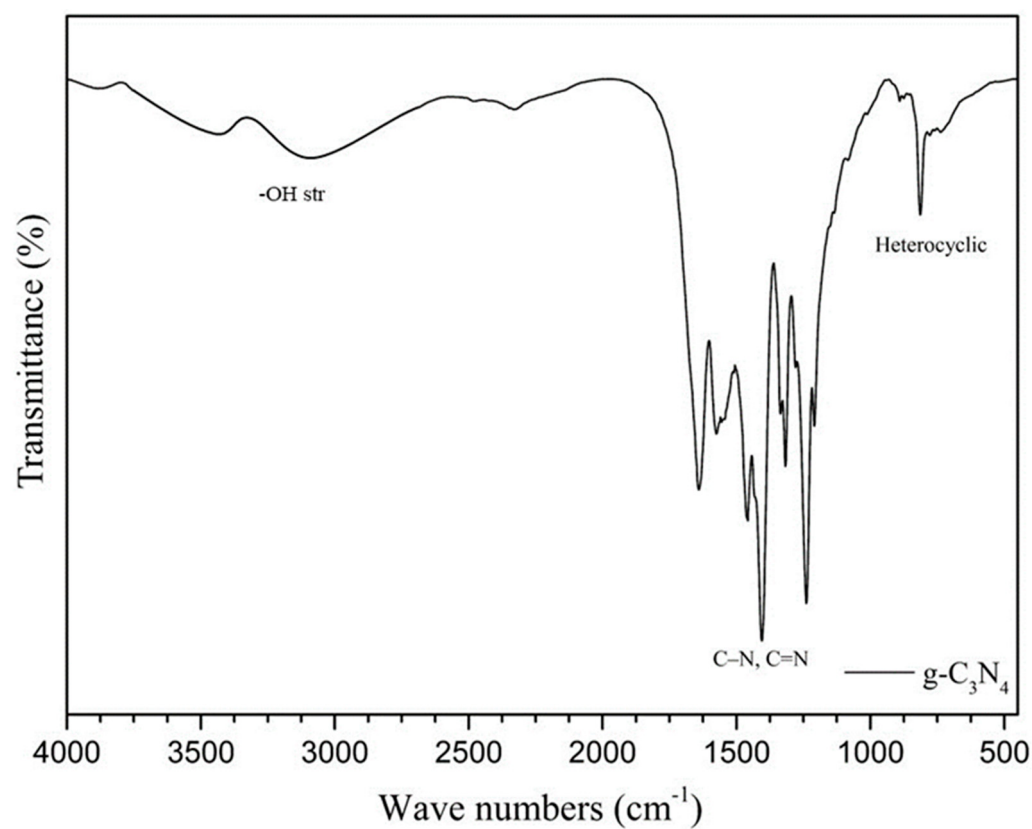


Figure 14. $g\text{-C}_3\text{N}_4$ FTIR spectra.

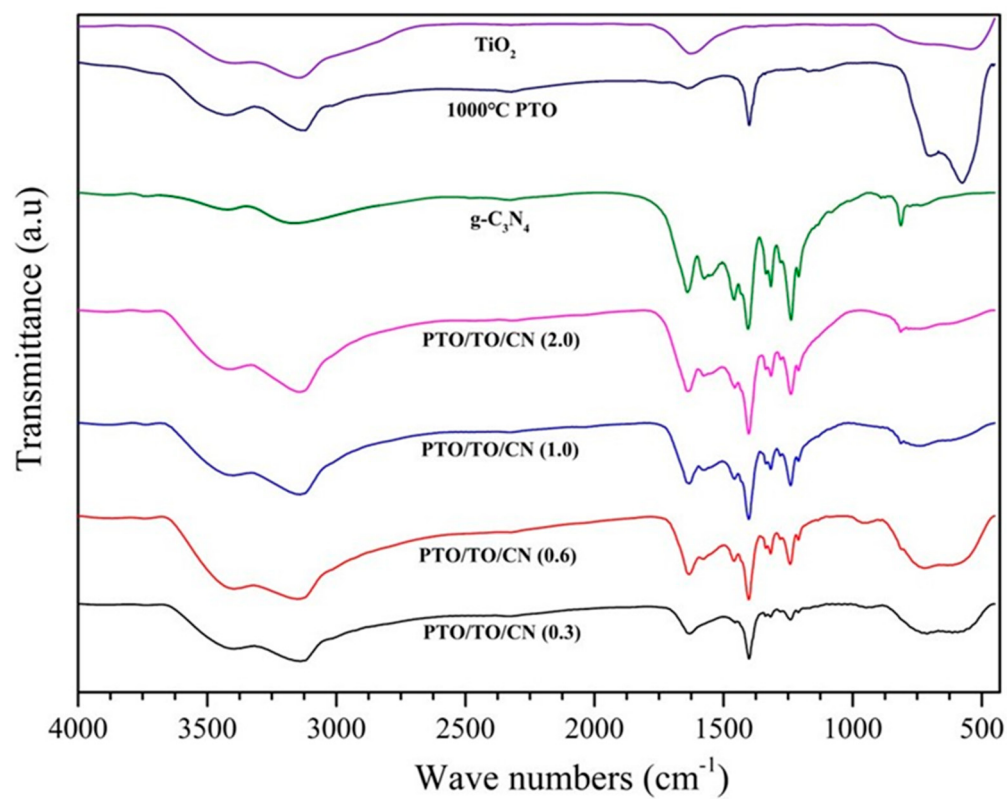


Figure 15. FTIR spectra of TiO_2 , 1000 °C PTO, $g\text{-C}_3\text{N}_4$, and PTO/TO/CN in various ratios.

3.4. Measurement and Analysis of BET

To better assess the adsorption capacity of different photocatalysts, N_2 adsorption–desorption tests were conducted using the BET method to measure particle size range and specific surface area. Among the photocatalysts tested, PTO/TO/CN (1.0) exhibited the highest visible light photocatalytic efficiency.

Figure 16 illustrates the isothermal adsorption–desorption curves of TiO_2 , 0.3 PTO/TO, and PTO/TO/CN (1.0). It can be observed that the adsorption–desorption isotherms of PTO/TO were higher than those of TiO_2 , indicating a superior dispersion of TiO_2 particles and an increased specific surface area, due to the addition of $PbTiO_3$. This also enhanced the N_2 adsorption capacity of PTO/TO. The adsorption–desorption isotherms of PTO/TO/CN (1.0) were higher than those of 0.3 PTO/TO across all pressure ranges. The addition of $g-C_3N_4$ facilitated the dispersion of PTO/TO particles on the surface of the $g-C_3N_4$, and the porous nature of the $g-C_3N_4$ allowed for the growth of PTO/TO microcrystals within its micropores, enabling N_2 adsorption. Additionally, the presence of $g-C_3N_4$ promoted the formation of mesoporous structures, further enhancing N_2 adsorption. The mesoporous structure between $g-C_3N_4$ also facilitated N_2 adsorption.

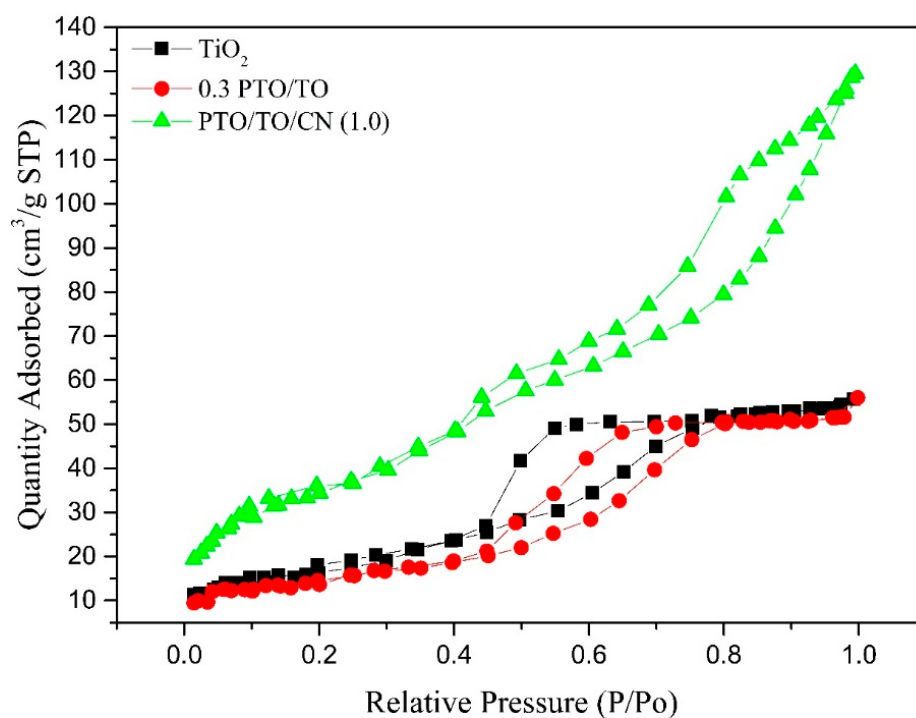


Figure 16. N_2 adsorption–desorption isotherms of TiO_2 , 0.3 PTO/TO, and PTO/TO/CN (1.0).

Figure 17 illustrates the isothermal adsorption–desorption curves of PTO/TO/CN (0.3), PTO/TO/CN (0.6), PTO/TO/CN (1.0), and PTO/TO/CN (2.0). As the amount of $g-C_3N_4$ increased, the curves gradually rose in the medium and high-pressure ranges, with PTO/TO/CN (2.0) exhibiting the highest curve. This can be attributed to the porous nature of $g-C_3N_4$, allowing for the growth of PTO/TO microcrystals within its micropores.

Figure 18 illustrates the pore size distribution curves of TiO_2 , 0.3 PTO/TO, and PTO/TO/CN (1.0). TiO_2 exhibited a pore size distribution between 2 and 10 nm, while 0.3 PTO/TO had a range of 3–11 nm. The doping of $PbTiO_3$ affected the growth and aggregation behavior of nanoscale particles during the sol-gel process, resulting in both larger pore sizes and changes in the pore volume ratio and size distribution of TiO_2 .

PTO/TO/CN (1.0) exhibited a broader pore size distribution and had a greater number of micropores compared to the 0.3 PTO/TO. The addition of $g-C_3N_4$ promoted the formation of a special structure, with PTO/TO particles on the surface of the $g-C_3N_4$, leading to smaller PTO/TO particles and a smaller mesopore size. This also contributed to

the larger specific surface area of PTO/TO/CN (1.0), compared to 0.3 PTO/TO. Figure 19 shows that PTO/TO/CN (1.0) had the largest pore size range of 1–120 nm. This is possibly due to the presence of special structured crystals with indentations.

Additionally, Table 5 presents a comparison of the specific surface areas made with each PTO/TO/CN sample. PTO/TO/CN (1.0) exhibited the highest specific surface area among the samples. This is likely due to the presence of special structured crystals with indentations, resulting in larger pore sizes and the widest pore size distribution.

Table 5. Sample specific surface area for different g-C₃N₄ weight ratios.

Sample	Specific Surface Areas (m ² /g)
TiO ₂	57.6802
0.3 PTO/TO	50.6191
PTO/TO/CN 2.0	135.4243
PTO/TO/CN 1.0	181.2409
PTO/TO/CN 0.3	147.1653
PTO/TO/CN 0.6	125.7055

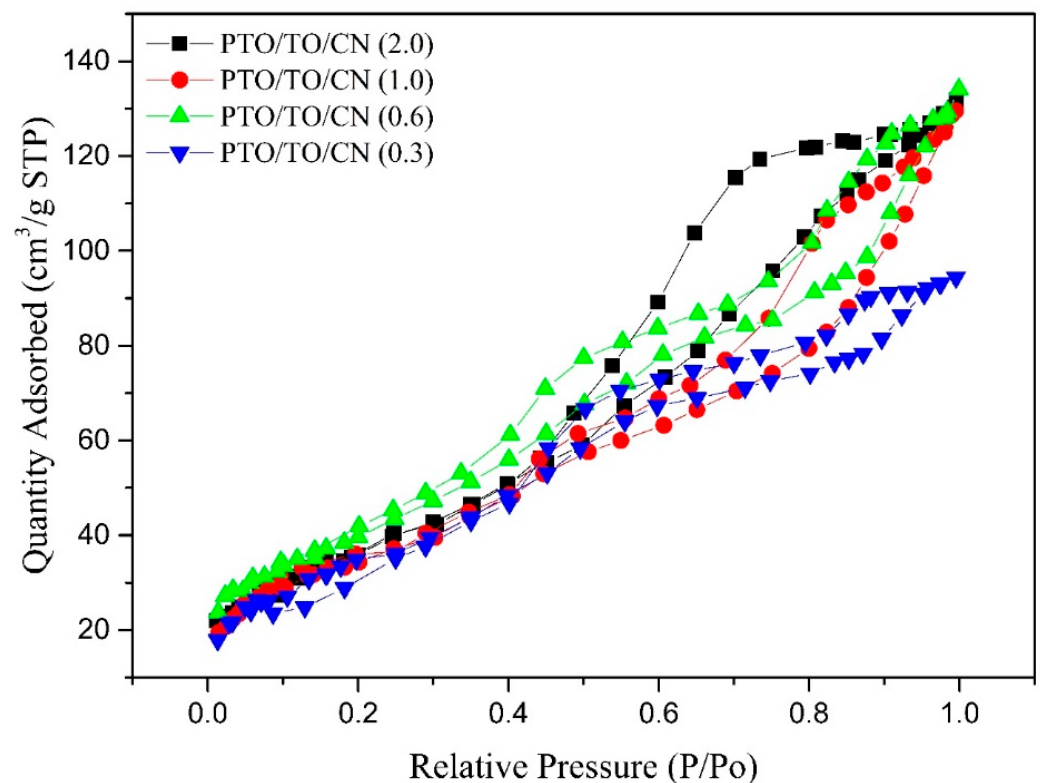


Figure 17. PTO/TO/CN (0.3), PTO/TO/CN (0.6), PTO/TO/CN (1.0), and PTO/TO/CN (2.0) isotherm adsorption-desorption curves.

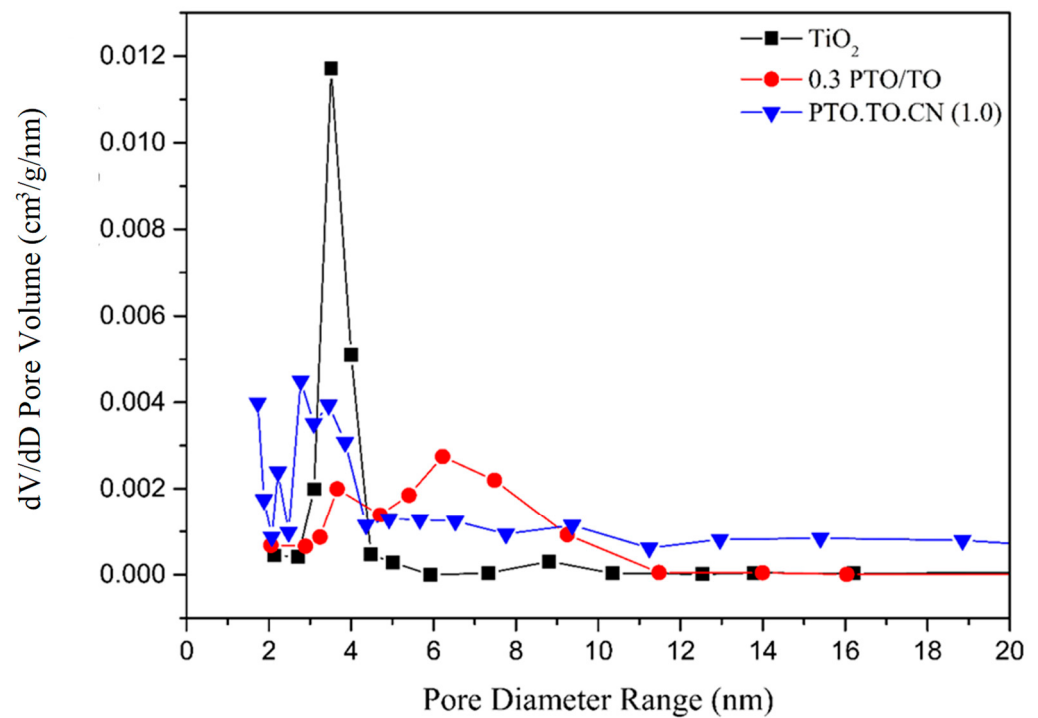


Figure 18. Pore size distribution curves of TiO_2 , 0.3 PTO/TO, and PTO/TO/CN (1.0).

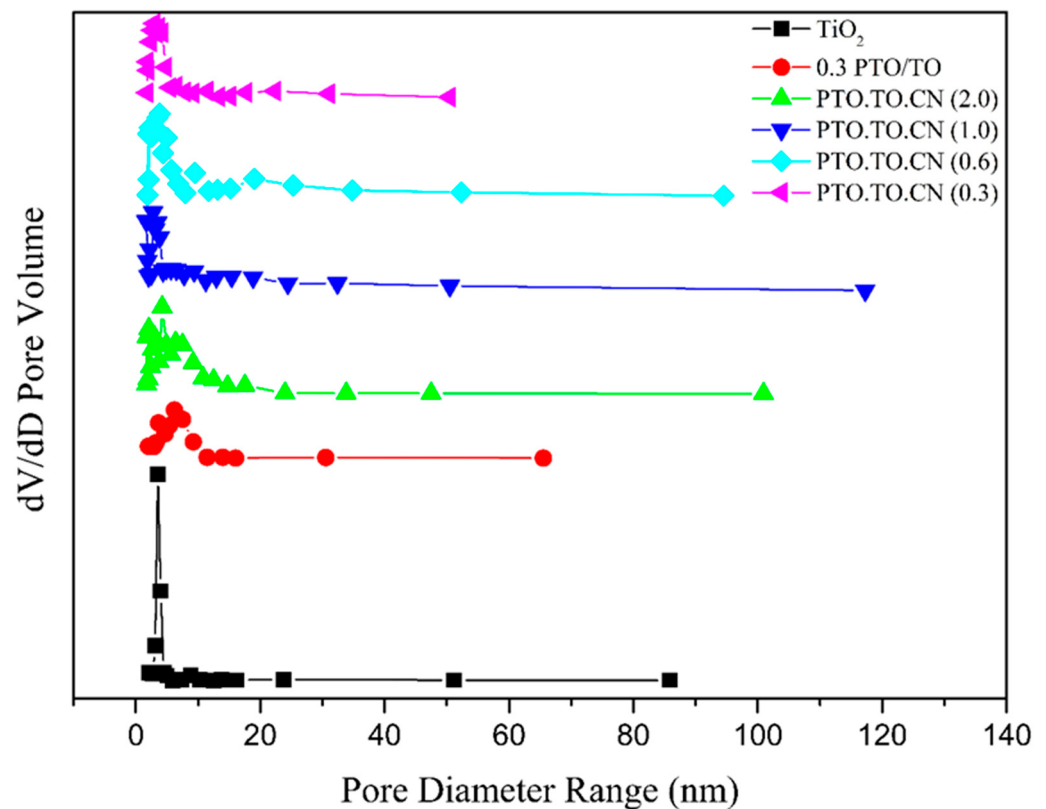


Figure 19. Pore size range distribution curves of TiO_2 and 0.3 PTO/TO for different weight ratios of PTO/TO/CN.

3.5. MB Removal via PTO/TO/CN Adsorption under Dark and Visible Light Photodegradation

A 0.01 g quantity of each photocatalyst was placed in 10 mL of 10 ppm MB solution. A 30 min dark adsorption period followed, and then the sample was exposed to 3 h of visible

light (irradiation photodegradation). The MB concentration change was measured every 30 min during testing and the experimental data were converted to an efficiency rating using Formulas (3) to (5).

C_d is the concentration of the dark adsorption experiment, C_l is the concentration of the visible light irradiation photodegradation experiment, and C_0 is the initial concentration of methylene blue. A_d is the dark adsorption efficiency, A_l is the photodegradation efficiency, and A_t is the summed photocatalytic efficiency.

$$A_d(\text{Dark Adsorption rate}) = \frac{C_d}{C_0} \times 100 \quad (4)$$

$$A_l(\text{Daylight Photodegradation rate}) = \frac{C_l}{C_0} \times 100\% \quad (5)$$

$$A_t(\text{Total Photocatalytic rate}) = A_d + A_l \quad (6)$$

The residual rate of MB degradation due to PTO synthesized at different temperatures is shown in Figure 20. Under dark adsorption for 30 min, followed by visible light irradiation for 3 h, the MB residual ratios for 700 °C PTO, 800 °C PTO, 900 °C PTO, and 1000 °C PTO were $78.40 \pm 0.46\%$, $78.06 \pm 0.57\%$, $76.06 \pm 0.25\%$, and $57.38 \pm 0.13\%$, respectively. Among these samples, the lowest residual rate of 1000 °C PTO was $57.38 \pm 0.13\%$, and its total removal rate was the highest, up to $42.62 \pm 5.58\%$, making it the superior PTO for MB removal in this batch of samples.

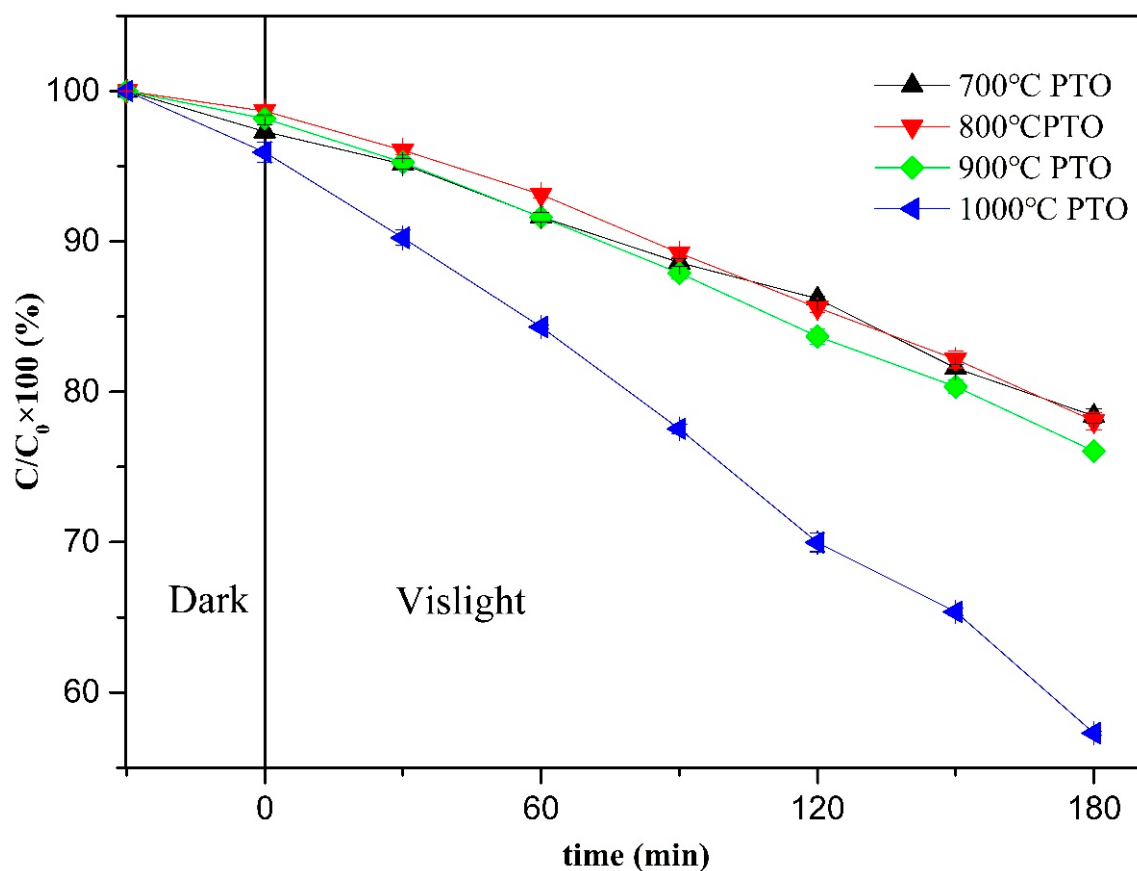


Figure 20. Photodegradation efficiency diagram of PTO synthesized at different temperatures.

Next, the residual rate of MB degradation by a composite photocatalyst PTO/TO with different ratios was examined. Figure 21 shows that, under dark adsorption for 30 min and visible light irradiation for 2.5 h, the MB residual ratios of 1 PTO/TO, 0.5 PTO/TO,

0.3 PTO/TO, and 0.1 PTO/TO were $72.06 \pm 0.32\%$, $67.27 \pm 0.57\%$, $42.53 \pm 9.61\%$, and $82.88 \pm 0.09\%$, respectively. Among these samples, the lowest residual rate of 0.3 PTO/TO was $42.53 \pm 9.61\%$. Thus, the highest total removal rate of MB by PTO/TO was $57.47 \pm 9.61\%$. It is concluded that adding PTO to TiO_2 can increase the photocatalytic effect, but the addition should not be excessive.

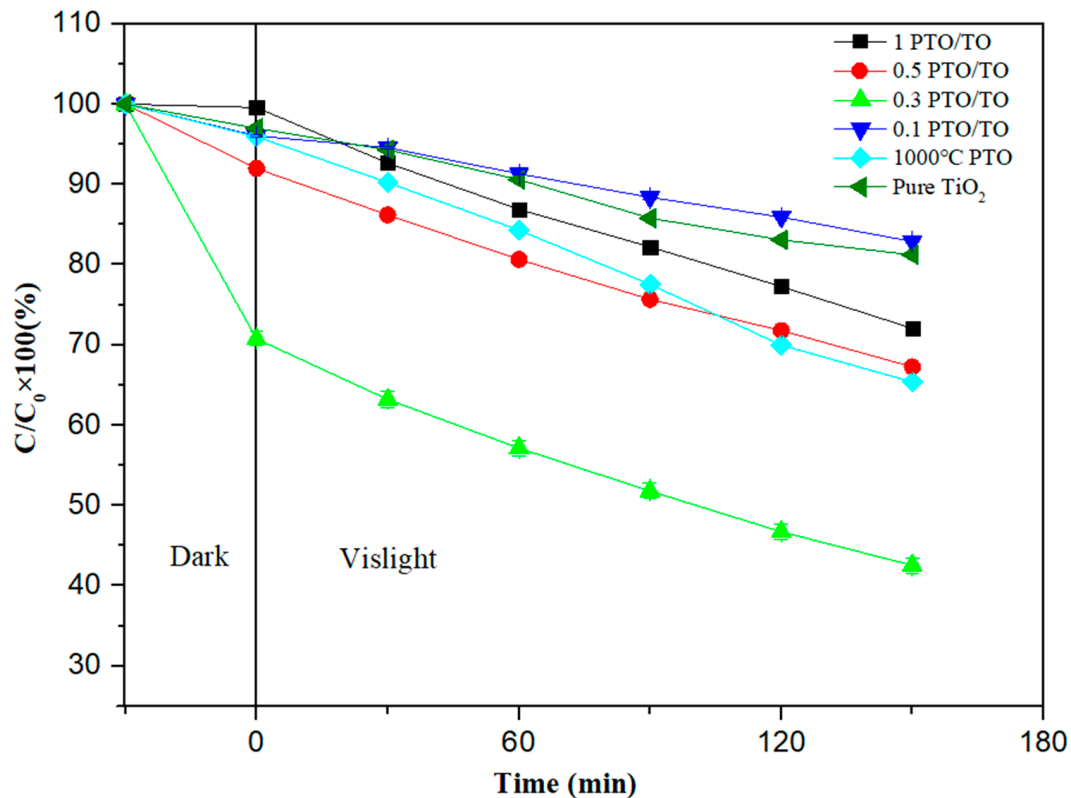


Figure 21. Photodegradation efficiency of different PTO/TO ratios.

Taking the optimal 0.3PTO/TO ratio, a new photocatalyst doped with different g- C_3N_4 weights was synthesized, creating PTO/TO/CN. The residual MB degradation rate is shown in Figure 22, where it can be seen that residual MB ratios for PTO/TO/CN (2), PTO/TO/CN (1), PTO/TO/CN (0.6), and PTO/TO/CN (0.3), under dark adsorption for 30 min and visible light irradiation for 2.5 h, were $1.66 \pm 0.00\%$, $2.49 \pm 0.00\%$, $1.21 \pm 0.02\%$, and $1.62 \pm 0.01\%$, respectively. The dark period adsorption effect appears notably improved, and the MB residual ratios reached $8.02 \pm 0.008\%$, $1.97 \pm 0.002\%$, $6.07 \pm 0.001\%$, and $10.26 \pm 0.006\%$, respectively.

Of the observed values, the lowest residual rate was provided by PTO/TO/CN (1), $1.21 \pm 0.02\%$; this means that that total removal rate was 98.79% , removing almost all of the MB from the water sample. Therefore, this was considered the optimal PTO/TO/CN ratio in this part of the experiment for the removal of MB. The degradation experiment results were verified through SEM. PTO/TO/CN was able to adsorb MB using its pores, and then continued to decompose due to its photodegradation characteristics.

Finally, a comparison of P25 was made with various photocatalysts, as shown in Figure 23. This figure shows how residual rates of MB change during treatment with P25, TiO_2 , 1000°C PTO, 0.3 PTO/TO, and PTO/TO/CN (1) under dark adsorption for 30 min, then visible light irradiation for 3 h, where the residuals were $77.10 \pm 0.24\%$, $79.83 \pm 0.52\%$, $57.29 \pm 0.13\%$, $38.35 \pm 9.38\%$, and $1.18 \pm 0.03\%$, respectively.

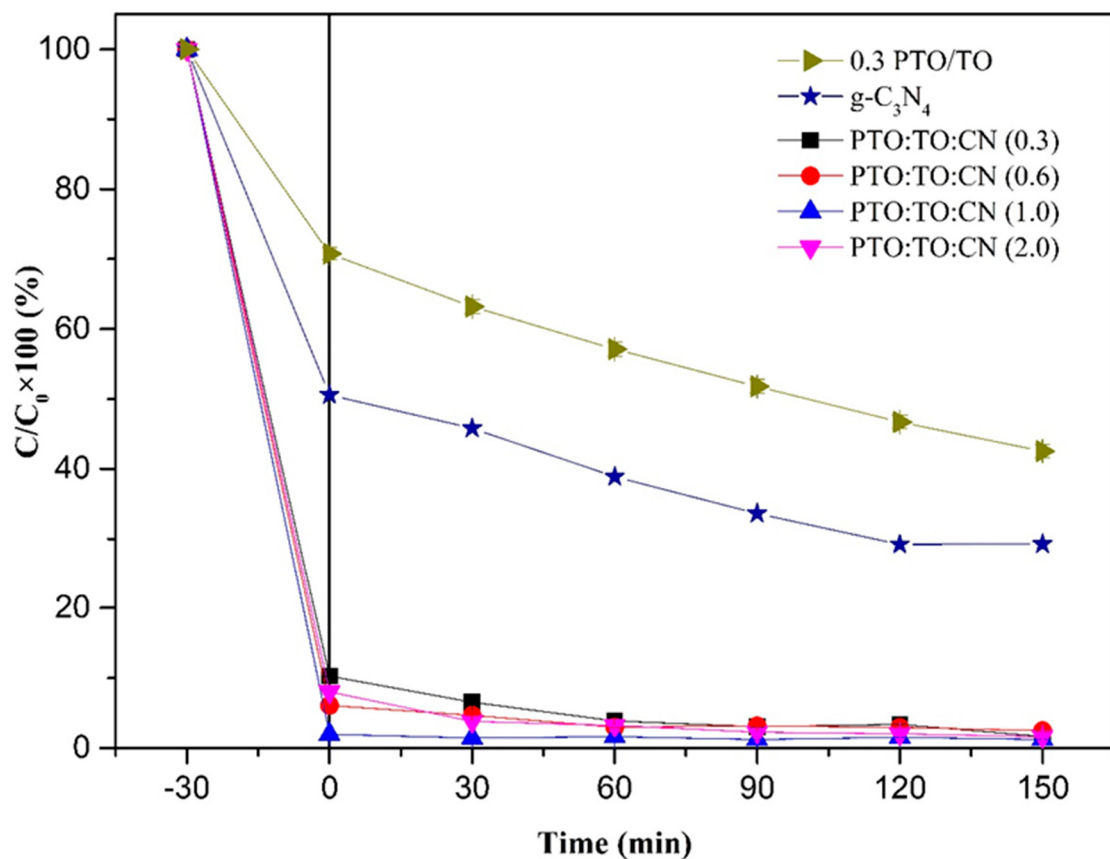


Figure 22. Photodegradation efficiency of PTO/TO/CN doped with different $g-C_3N_4$ weights.

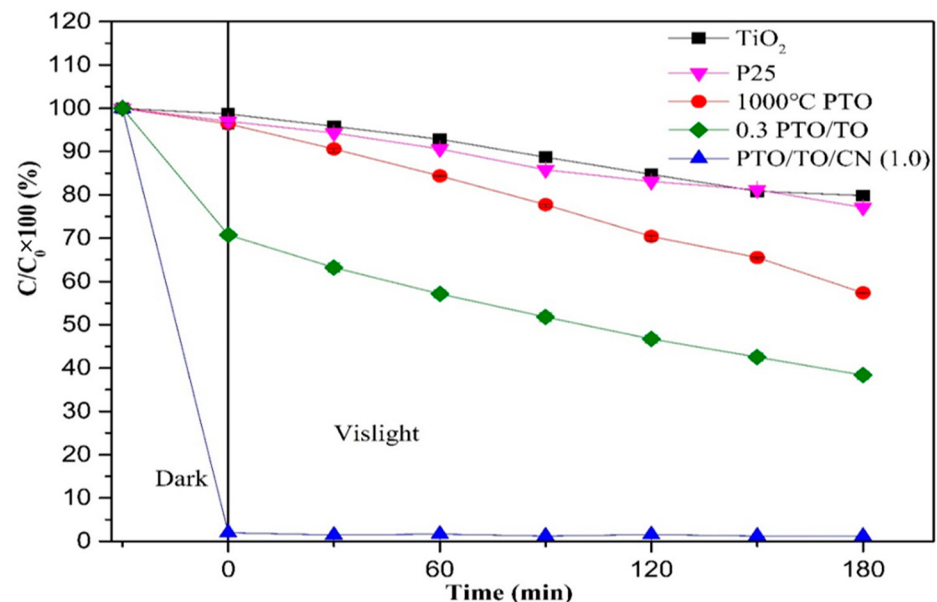


Figure 23. MB degradation efficiency of TiO_2 , P25, 1000 °C PTO, 0.3 PTO/TO, and PTO/TO/CN (1) under 30 min of darkness and 3 h of visible light.

The removal rate of MB after degradation under visible light for 3 h is shown in Figure 24. The degradation effect of TiO_2 was equivalent to that of P25, but the addition of PTO improved the degradation effect under visible light. This is because the P-type semiconductor heterostructure was formed by coupling two components, and this generated a “built-in” electrical field at the junction interface; this enhanced charge separation and

facilitated the reverse transfer of electrons and holes to different components. The value of the valance band (VB) also changed, from 2.91 eV to 0.27 eV, as shown in Figure 25.

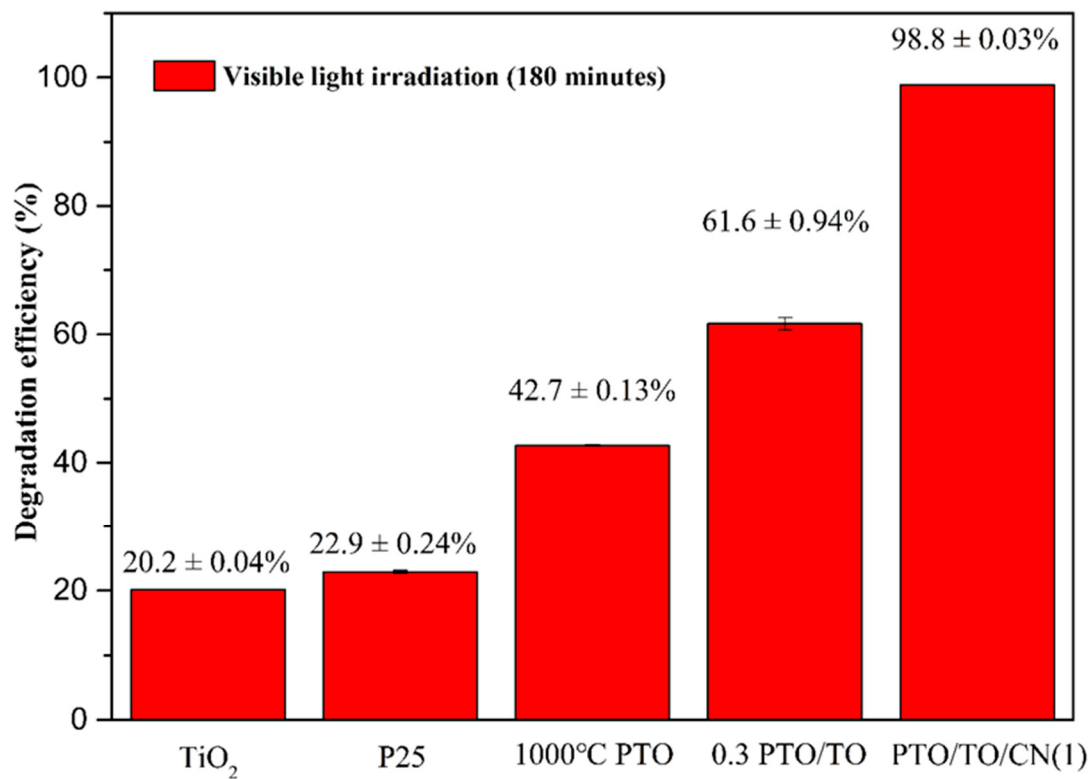


Figure 24. MB removal rates of TiO₂, P25, 1000 °C PTO, 0.3 PTO/TO, and PTO/TO/CN (1) under visible light for 3 h.

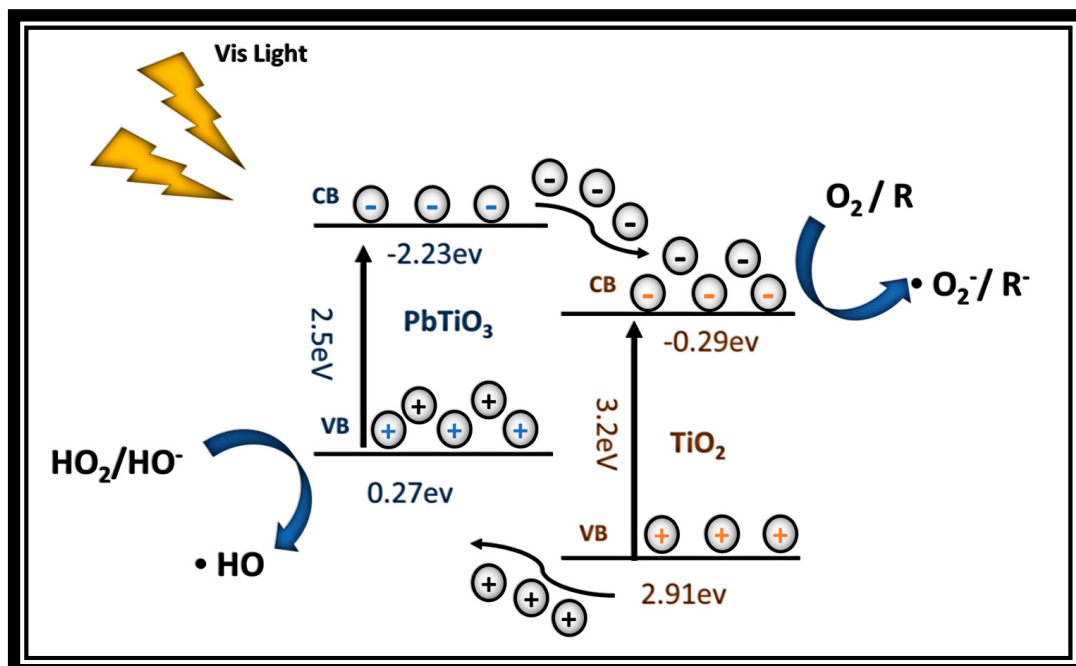


Figure 25. Schematic diagram of energy-carrying electron transfer in the bandgap structure of the PTO/TO composites.

This is because the CB edge potential of PbTiO₃ (−2.23 eV vs. NHE) is more negative than that of TiO₂ (−0.29 eV vs. NHE). The large potential difference between the CB edges of PbTiO₃ and TiO₂ promoted electron transfer from PbTiO₃ to TiO₂, enhancing the separation of photo-induced charge carriers and the corresponding photocatalytic activity. Both the CB edges of PbTiO₃ and TiO₂ were more negative than the oxidation-reduction potential of the O₂/O₂[−] couple (−0.046 eV vs. NHE), allowing the adsorbed O₂ to react with the electrons on the CBs of PbTiO₃ and TiO₂ to generate superoxide radicals. On the other hand, the photo-generated positive holes remained in the VB of PbTiO₃. Since the VB edge potential of PbTiO₃ (+0.27 eV vs. NHE) was lower than the oxidation-reduction potentials of the ·OH/OH[−] couple (+1.99 eV vs. NHE) and the ·OH/H₂O couple (+2.68 eV vs. NHE), the strong potential difference between the CB edges of PbTiO₃ and TiO₂ promoted electron transfer from PbTiO₃ to TiO₂, reacting with OH[−] or H₂O to generate highly reactive hydroxyl radicals [35,36].

A UV-Vis spectrophotometer was used to test the absorbance of the materials. In this study, the absorption wavelengths of TiO₂, 700 °C PTO, 800 °C PTO, 900 °C PTO, and 1000 °C PTO were examined, and wavelength measurements were taken in the range 200–800 nm. As shown in Figure 26a,b, Equation (7) was used to convert the absorption spectrum into a Tauc plot. The Tauc plot curve on the X-axis was extrapolated to obtain the energy gap values. In Equation (7), α is the absorption coefficient, h is Planck's constant, ν is the photon frequency, A is a constant, and E_g is the energy gap. In this study, because PpTiO₃ and TiO₂ are indirect band gaps, the value of n is 2.

$$\alpha h\nu = A(h\nu - E_g)^n \quad (7)$$

The calculated energy gaps of TiO₂, 700 °C PTO, 800 °C PTO, 900 °C PTO, and 1000 °C PTO were recorded as 3.2 eV, 2.62 eV, 2.59 eV, 2.57 eV, and 2.51 eV, respectively. Figure 27a,b shows that as the synthesis temperature increased, the PTO energy gap became smaller, and the crystallinity improved the electronic transition. This was used to verify the results of the MB degradation experiments. The experimental results in the visible light wavelength range 390–800 nm showed that changes within that range yielded different results for PTO/TO photocatalysts with different weight ratios. The 0.3 PTO/TO exhibited the highest visible light absorption, as shown in Figure 28b. Converting the UV-Vis absorption of 1 PTO/TO, 0.5 PTO/TO, 0.3 PTO/TO, and 0.1 PTO/TO photocatalysts into Tauc diagrams, the energy gap values were 2.6 eV, 2.3 eV, 2.25 eV, and 2.46 eV, respectively. The photocatalyst with 0.3 PTO/TO had the lowest energy gap, and this was consistent with the prior degradation experiments.

Figure 29 shows that PTO/TO/CN (1) had the highest visible light absorption, and the converted energy gap value was 2.59 eV. This corresponded to the dye removal experiment, where the better the visible light absorption, the better the photocatalytic effect. Therefore, the absorbance influences the photocatalytic effect, and cannot be judged only by the smaller energy gap.

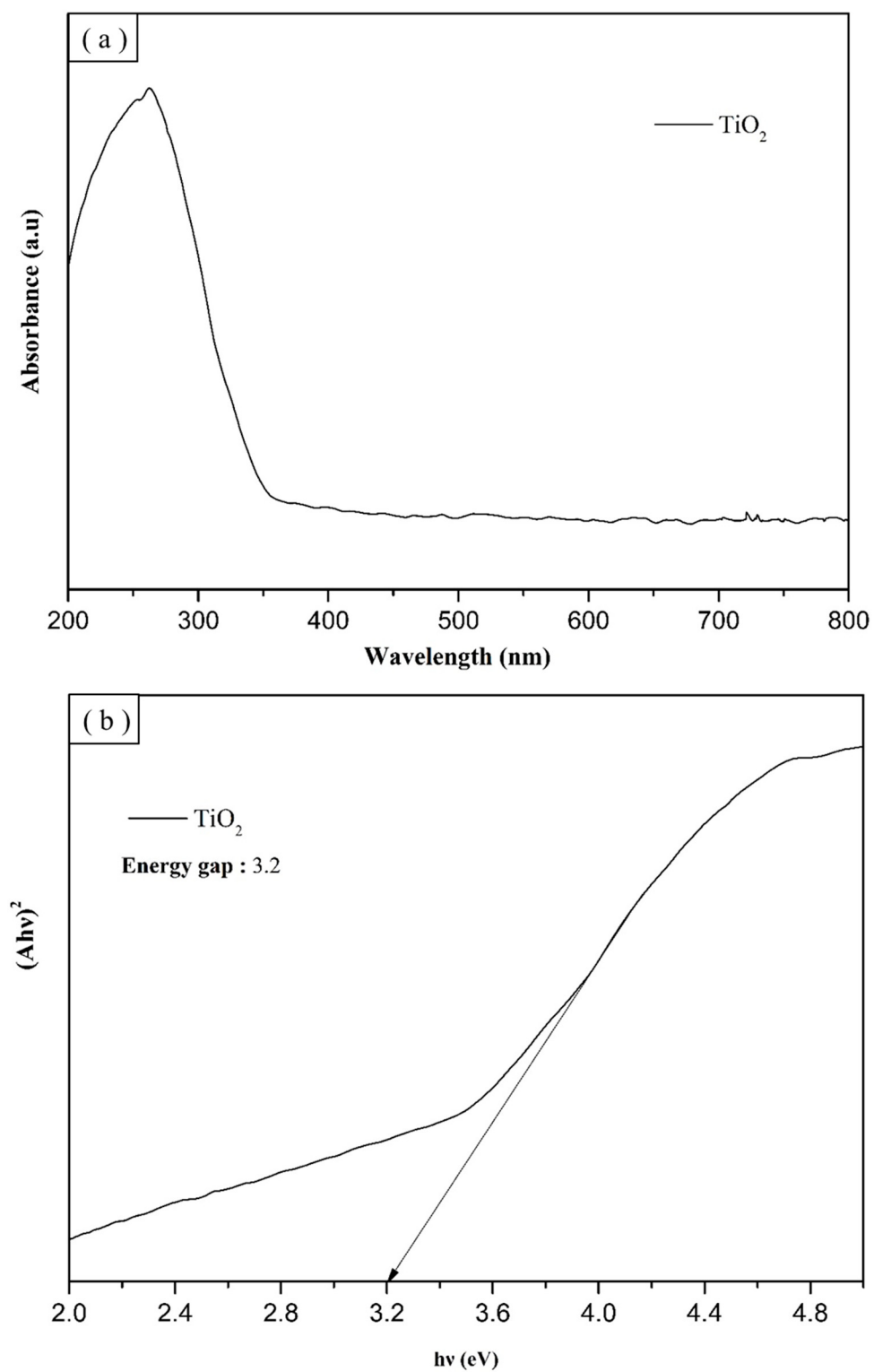


Figure 26. (a) UV-Vis absorption spectrum of TiO_2 , and (b) TiO_2 Tauc plot.

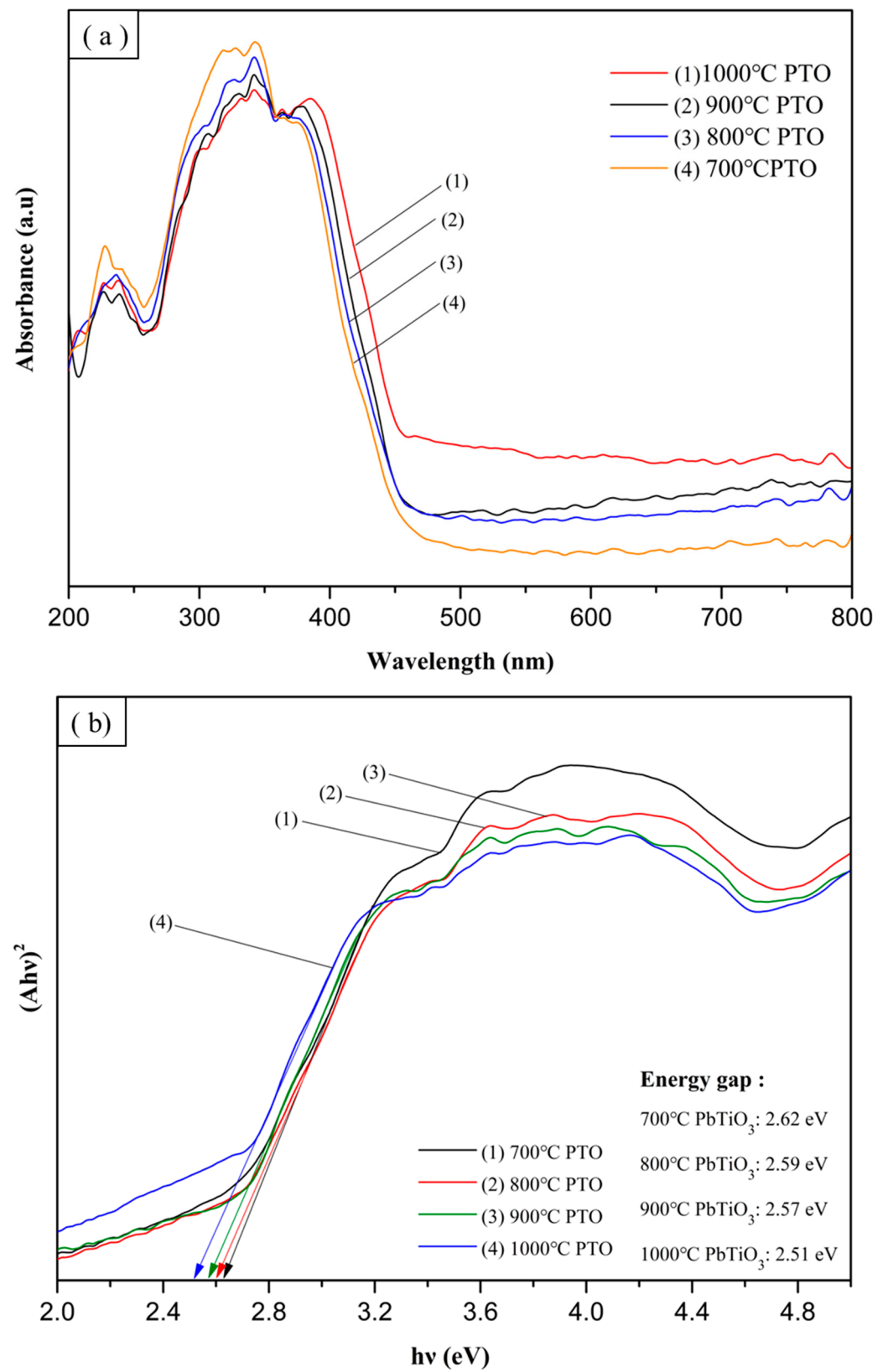


Figure 27. (a) UV-Vis absorption spectrum PbTiO_3 sintered at different temperatures, and (b) PbTiO_3 Tauc plot.

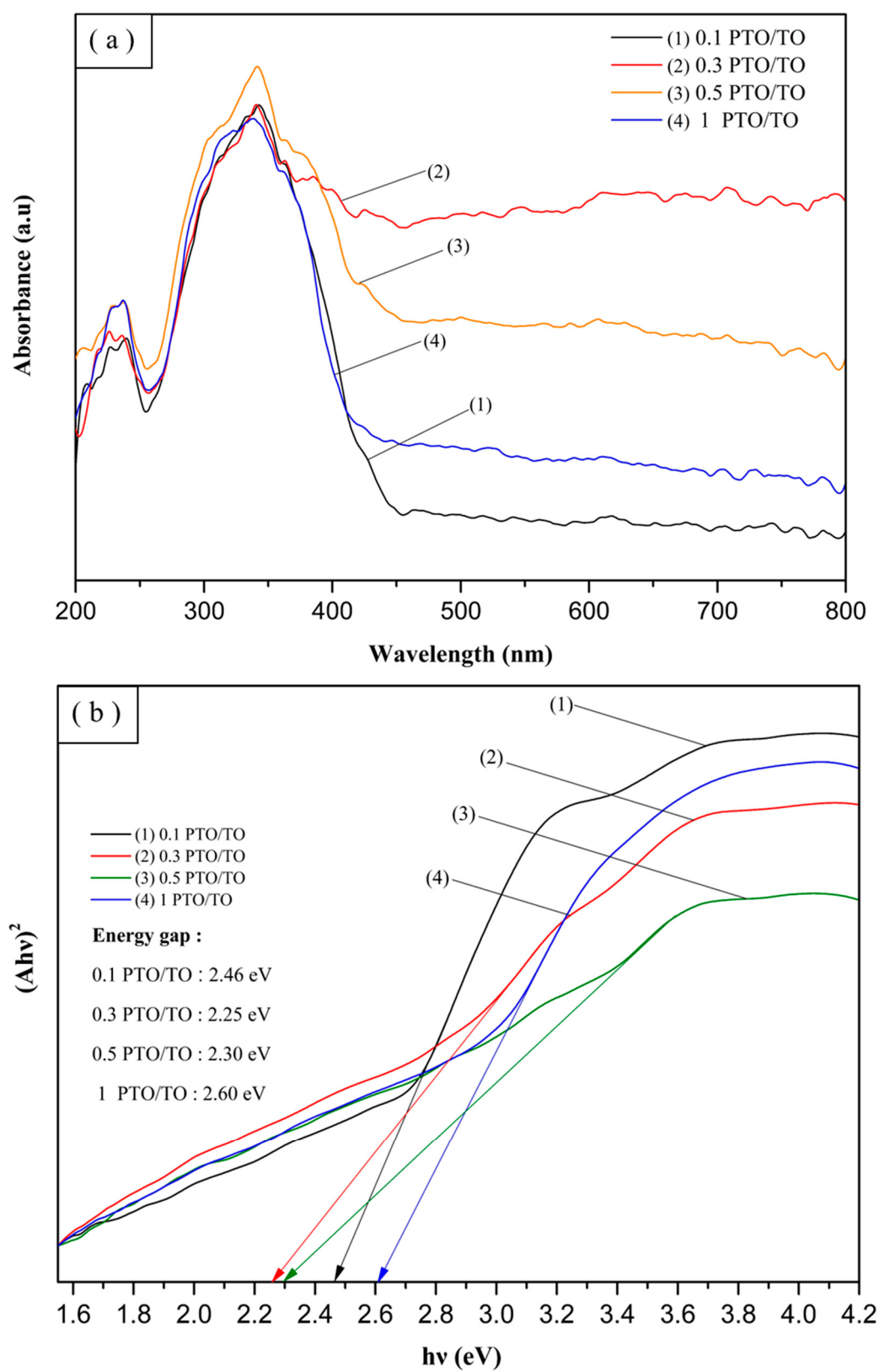


Figure 28. (a) UV-Vis absorption spectra for different PTO/TO ratios and (b) Tauc plots of different ratios of PTO/TO.

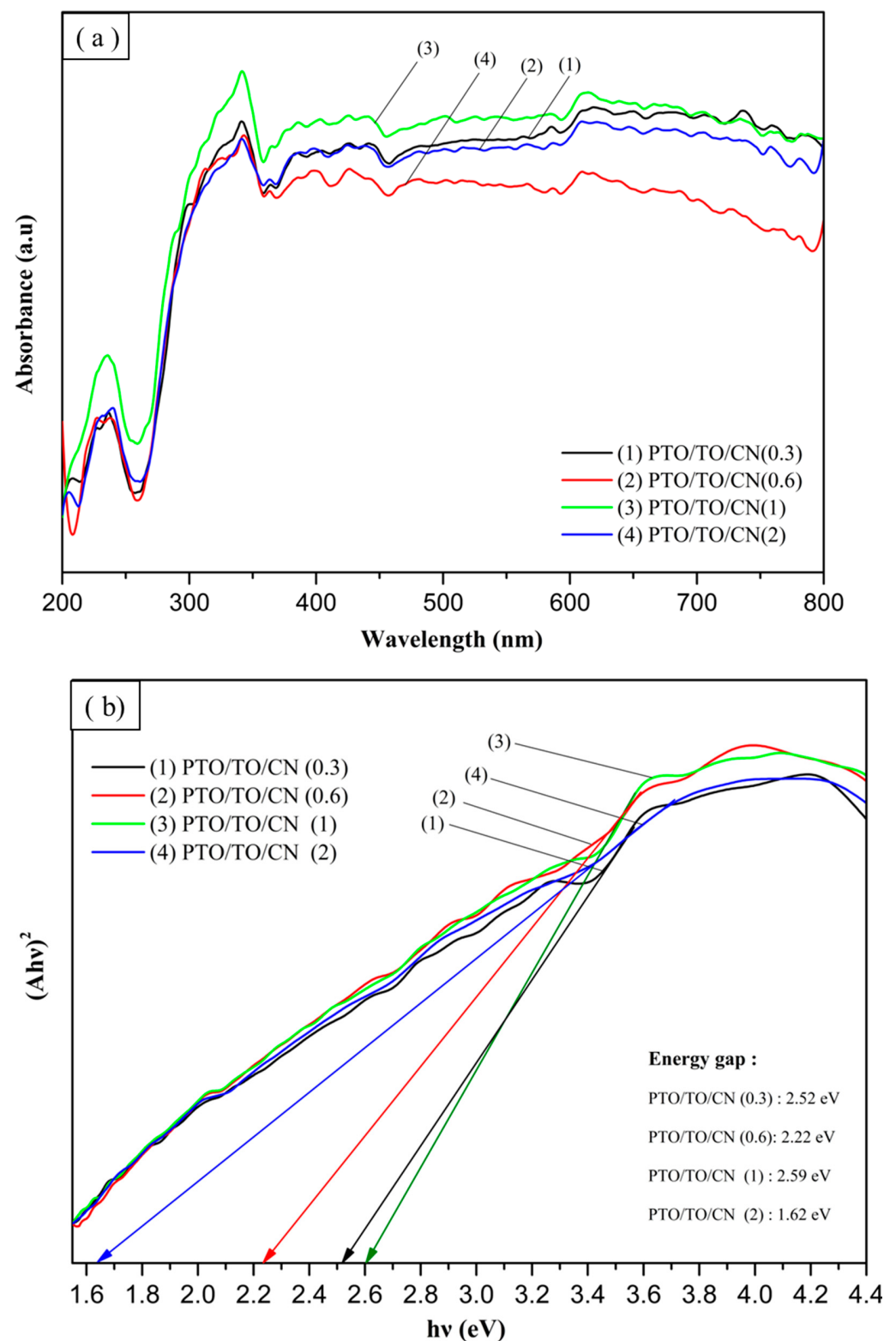


Figure 29. (a) UV-Vis absorption spectra of different PTO/TO/CN ratios and (b) Tauc plots of different PTO/TO/CN ratios.

4. Conclusions

PbTiO₃ was successfully synthesized using a self-made ball mill via the solid-state reaction method. The optimal calcination temperature was determined to be 1000 °C. The XRD and SEM results showed that the 1000 °C PTO sample exhibited the highest

crystallinity, and also exhibited the highest MB removal rate under visible light, compared to other PbTiO₃ samples. The XRD and SEM analysis demonstrated that PTO/TO/CN (1.0) had particles with special structures, and a smaller particle size than other combinations. The BET analysis of PTO/TO/CN (1.0) showed that it had the largest specific surface area, and this was attributed to the special structure of the small particles and surface irregularities, enabling it to adsorb a large amount of MB. Additionally, g-C₃N₄ exhibited a notable visible light response, further enhancing the visible light absorption of PTO/TO/CN (1.0). Experiments compared the widely used and commercially available P25 photocatalyst to the PTO/TO/CN (1.0) photocatalyst synthesized during this study. The PTO/TO/CN (1.0) sample exhibited significantly superior adsorption performance, even surpassing TiO₂ in terms of visible light response. This study successfully developed a photocatalyst with high adsorption capacity, and the ability to degrade organic substances under visible light irradiation.

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