



## Facile Control of Anatase-Rutile Phase Ratio in TiO<sub>2</sub> Nanoparticles for Highly Efficient Photocatalytic Degradation of Methylene Blue

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### Article Info

#### Article type:

Research Article

#### Article history:

Received: 11 May 2026

Revised: 6 Jul 2026

Accepted: 23 Sep 2026

#### Keywords:

TiO<sub>2</sub> nanoparticle

Phase control

Anatase-Rutile

heterojunction

Photocatalysis

Methylene Blue

### ABSTRACT

Spherical TiO<sub>2</sub> nanoparticles with tunable phase compositions were successfully synthesized via a one-step hydrothermal method by modulating HNO<sub>3</sub> dosage. The results reveal that acidity plays a decisive role in governing nucleation kinetics, particle size, and phase evolution from pure rutile to anatase-rutile mixed structures. XRD analysis confirms a transition from 100% rutile (1 mL HNO<sub>3</sub>) to the most effective mixed-phase composition (62.8% anatase/37.2% rutile at 3 mL and 73.7% anatase/26.3% rutile at 5 mL). This structural evolution is accompanied by particle size refinement from 14.1 nm to 12 nm and enhanced surface hydroxylation. Optical studies show that the 3-HNO<sub>3</sub> sample exhibits the lowest photoluminescence intensity and a reduced bandgap (3.05 eV), indicating efficient charge separation. As a result, this sample delivers superior photocatalytic performance, achieving 99% Methylene Blue removal within 150 min under UV irradiation, with a high apparent rate constant of 0.028 min<sup>-1</sup>. The enhanced activity is attributed to the synergistic effect of optimized anatase-rutile heterojunctions and nanoscale size control, which promote interfacial charge transfer and suppress electron-hole recombination. This work provides a simple yet effective strategy for phase engineering of TiO<sub>2</sub> toward high-performance photocatalytic applications.

**Cite this article:** Xuan Quang, N., Van Manh, T., Van Toi, N., Van Quang, N., Thi Yen, L., Van Hoang, O., & Quoc Tuan, T. (2026). Facile Control of Anatase-Rutile Phase Ratio in TiO<sub>2</sub> Nanoparticles for Highly Efficient Photocatalytic Degradation of Methylene Blue. *Pollution*, 12(4), 1010-1025.  
<https://doi.org/10.22059/poll.2026.414221.3330>



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Publisher: The University of Tehran Press.

DOI: <https://doi.org/10.22059/poll.2026.414221.3330>

## INTRODUCTION

The continuous expansion of industrial activities has led to the persistent release of refractory organic pollutants into aquatic environments, posing long-term risks to ecological systems and public health. Among these contaminants, synthetic dyes from textile, printing, and pharmaceutical industries are particularly problematic due to their complex aromatic structures, high chemical stability, and resistance to conventional biological treatments (Rafatullah et al., 2010; Lellis et al., 2019). Methylene Blue (MB), a widely used cationic dye, is frequently employed as a model compound to evaluate photocatalytic performance because of its recalcitrant nature and well-defined spectroscopic characteristics (Chekir et al., 2016). The effective mineralization of such pollutants into harmless end products remains a central challenge in environmental remediation.

In recent years, semiconductor-based photocatalysis has emerged as a key component of advanced oxidation processes (AOPs), offering a sustainable route for pollutant degradation

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driven by solar or artificial irradiation. Among various photocatalysts,  $\text{TiO}_2$  continues to serve as a benchmark material due to its chemical stability, low toxicity, and strong oxidative capability (Anucha et al., 2022; H. Khan & Shah, 2023). However, the practical efficiency of pristine  $\text{TiO}_2$  is fundamentally limited by the ultrafast recombination of photogenerated electron-hole pairs and its suboptimal utilization of photogenerated charge carriers, which significantly restricts its quantum efficiency (H. Zhang & Banfield, 2000b).

A growing body of research has demonstrated that the photocatalytic performance of  $\text{TiO}_2$  is strongly dependent on its crystal phase composition. The two most common polymorphs, anatase and rutile, exhibit distinct electronic structures and surface properties. Anatase is generally regarded as the more photoactive phase due to its higher conduction band position, larger specific surface area, and superior surface hydroxylation, which favor redox reactions. In contrast, rutile is thermodynamically stable but typically suffers from faster charge recombination and lower surface reactivity (Luttrell et al., 2014). Importantly, recent advances highlight that neither phase alone is optimal; instead, the coexistence of anatase and rutile can generate a synergistic effect that significantly enhances photocatalytic efficiency.

This enhancement is primarily attributed to the formation of an anatase–rutile heterojunction, where the band alignment between the two phases facilitates directional charge transfer across the interface. Such interfacial charge migration promotes spatial separation of electrons and holes, effectively suppressing recombination and prolonging carrier lifetimes. This phenomenon has been widely observed in mixed-phase systems such as the commercial P25 photocatalyst, which consistently outperforms single-phase counterparts (Scanlon et al., 2013; Hurum et al., 2003; J. Zhang et al., 2014). Therefore, precise control over the anatase-to-rutile phase ratio has become a critical strategy in the design of high-performance  $\text{TiO}_2$ -based photocatalysts.

Among various synthesis approaches, the hydrothermal method offers a versatile and scalable route for tailoring the phase composition and morphology of  $\text{TiO}_2$  nanostructures under relatively mild conditions (Byrappa & Adschiri, 2007). In such systems, the hydrolysis and condensation kinetics of titanium precursors are highly sensitive to the chemical environment, particularly the acidity of the reaction medium. Nitric acid ( $\text{HNO}_3$ ) plays a crucial role not only as a peptizing agent but also as a kinetic modulator that governs nucleation, crystal growth, and phase transformation pathways. Although previous studies have acknowledged the influence of pH on  $\text{TiO}_2$  crystallization (Reyes-Coronado et al., 2008; Cargnello et al., 2014), a clear and systematic understanding of how the controlled variation of  $\text{HNO}_3$  dosage directs the evolution from single-phase rutile to optimized anatase–rutile heterostructures, and how this impacts photocatalytic activity—remains insufficiently explored.

In this work, we present a facile one-step hydrothermal strategy for the controlled synthesis of  $\text{TiO}_2$  nanoparticles with tunable phase compositions by adjusting the ratio of titanium butoxide to  $\text{HNO}_3$ . We demonstrate that the acid dosage acts as a decisive parameter governing both nucleation kinetics and phase evolution, enabling a transition from pure rutile to mixed-phase anatase–rutile structures. The resulting heterojunctions exhibit significantly enhanced photocatalytic performance toward Methylene Blue degradation under UV irradiation. This study provides new insights into phase-dependent photocatalysis and offers a simple yet effective approach for designing advanced  $\text{TiO}_2$ -based materials for environmental applications.

## MATERIAL AND METHODS

### *Chemicals*

Titanium(IV) butoxide ( $\text{Ti}(\text{OC}_4\text{H}_9)_4$ , 99.98%), Methylene Blue (MB, 99.98%) and Nitric acid ( $\text{HNO}_3$ , 37 wt%) were purchased from Sigma-Aldrich. Deionized (DI) water was employed for all solution preparations and washing procedures. All reagents were of analytical grade and used as received without further purification.

### *Synthesis of TiO<sub>2</sub> nanoparticles*

TiO<sub>2</sub> nanoparticles were synthesized via a facile one-step hydrothermal method. In a typical procedure, the hydrolysis of the titanium precursor was controlled by adjusting the acidity of the reaction medium. A predetermined volume of HNO<sub>3</sub> (1, 3, or 5 mL) was first mixed with deionized (DI) water to obtain a total solution volume of 60 mL. The acidic solution was magnetically stirred for 5 min to ensure complete homogenization. Subsequently, 1 mL of titanium(IV) butoxide (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>) was added dropwise into the solution under continuous stirring, followed by further stirring for 5 min to form a uniform precursor suspension.

The resulting mixture was then transferred into a Teflon-lined stainless steel autoclave and subjected to hydrothermal treatment at 100 °C for 24 h. After naturally cooling to room temperature, the precipitates were collected by centrifugation at 5000 rpm and washed twice with distilled water to remove residual ions and unreacted species. The products were subsequently pre-dried at 100 °C for 1 h in an oven. The obtained samples were labeled according to the volume of HNO<sub>3</sub> used during synthesis, namely 1-HNO<sub>3</sub>, 3-HNO<sub>3</sub>, and 5-HNO<sub>3</sub>.

### *Characterization*

The structural, morphological, and optical properties of the as-synthesized TiO<sub>2</sub> nanoparticles were systematically characterized using a combination of advanced analytical techniques. The crystalline phases were analyzed by X-ray diffraction (XRD, Siemens) using Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) operated at 40 kV and 30 mA, with a scanning range of  $2\theta$  = 10–80° and a step size of 0.02°. The morphology was examined by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) at an accelerating voltage of 5–15 kV, while the elemental composition and purity of the samples were confirmed by energy-dispersive X-ray spectroscopy (EDX) coupled with the FE-SEM system. Particle size distributions were obtained from SEM images. Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet iS10 spectrometer in the range of 400–4000 cm<sup>−1</sup> with a resolution of 4 cm<sup>−1</sup>. UV–Vis diffuse reflectance spectra (DRS) were measured using an Optima SP-3000 Nano spectrophotometer in the wavelength range of 200–800 nm, using BaSO<sub>4</sub> as a reference. Photoluminescence (PL) spectra were obtained using a fluorescence spectrophotometer with an excitation wavelength of 325 nm, and emission spectra were recorded in the range of 350–600 nm. The zeta potential was measured using Zetasizer Nano ZS to evaluate the surface charge of the photocatalysts at different pH values.

### *Evaluation of Photocatalytic Activity*

The photocatalytic activity of the as-prepared TiO<sub>2</sub> nanospheres was evaluated through the degradation of Methylene Blue (MB) under UV irradiation. In a typical experiment, 20 mg of the photocatalyst was dispersed in 30 mL of an aqueous MB solution with an initial concentration of 50 ppm in a 250 mL beaker. The suspension was magnetically stirred in the dark for 30 min prior to irradiation to establish adsorption-desorption equilibrium between the dye molecules and the catalyst surface.

Subsequently, the suspension was irradiated using a 40 W UV-lamp (Philips) with a peak emission wavelength of 365 nm to initiate the photocatalytic reaction. The light source was positioned at a fixed distance of 15 cm above the beaker to ensure uniform exposure. This constant irradiation intensity was maintained throughout the degradation experiments to ensure reproducible kinetic conditions. The degradation process was monitored over 150 min. At regular intervals of 30 min, aliquots were withdrawn and immediately centrifuged at 5000 rpm to remove the catalyst particles. The residual concentration of MB in the supernatant was determined by measuring its absorbance at the maximum absorption wavelength ( $\lambda_{\text{max}}$  = 664 nm) using a UV–Vis spectrophotometer.

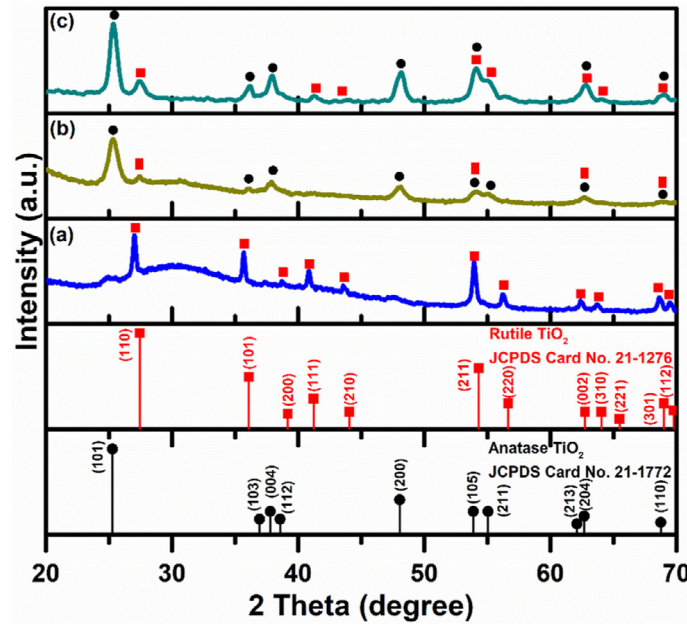


**Fig. 1.** X-ray diffraction (XRD) patterns of  $\text{TiO}_2$  nanoparticles synthesized with different  $\text{HNO}_3$  volumes: (a) 1 mL; (b) 3 mL; and (c) 5 mL

## RESULTS AND DISCUSSION

### Structure characterization

The crystalline phase composition and structural evolution of the  $\text{TiO}_2$  nanoparticles as a function of  $\text{HNO}_3$  dosage were investigated by X-ray diffraction (XRD), as shown in Fig. 1. The diffraction patterns clearly demonstrate a pronounced phase transformation governed by the acidity of the reaction medium.

For the sample synthesized with 1 mL  $\text{HNO}_3$  (Fig. 1a), the XRD pattern exhibits sharp diffraction peaks at  $2\theta \approx 27.4^\circ$ ,  $36.1^\circ$ ,  $41.2^\circ$ , and  $54.3^\circ$ , corresponding to the (110), (101), (111), and (211) planes of tetragonal rutile  $\text{TiO}_2$  (JCPDS No. 21-1276). No characteristic peaks of anatase are observed, confirming the formation of a pure rutile phase. Quantitative analysis further indicates that this sample consists of 100% rutile and 0% anatase, consistent with the dominance of the thermodynamically stable rutile phase under low-acidity conditions (Hanaor & Sorrell, 2011). When the  $\text{HNO}_3$  volume is increased to 3 mL (Fig. 1b), additional diffraction peaks at  $2\theta \approx 25.3^\circ$ ,  $37.8^\circ$ , and  $48.0^\circ$  emerge, corresponding to the (101), (004), and (200) planes of anatase  $\text{TiO}_2$  (JCPDS No. 21-1272). Meanwhile, the rutile peak at  $27.4^\circ$  remains present, indicating the coexistence of both phases. The phase composition was estimated using the Spurr–Myers equation:

$$X_A = \frac{1}{1 + 1.26 \left( \frac{I_R}{I_A} \right)} \quad (1)$$

Where  $X_A$  is the weight fraction of anatase, and  $I_A$  and  $I_R$  are the intensities of the anatase (101) and rutile (110) peaks, respectively. Based on this calculation, the sample contains 62.8% anatase and 37.2% rutile, confirming the formation of a mixed-phase structure. This transition can be attributed to the increased hydrolysis rate under higher acidity, which promotes rapid

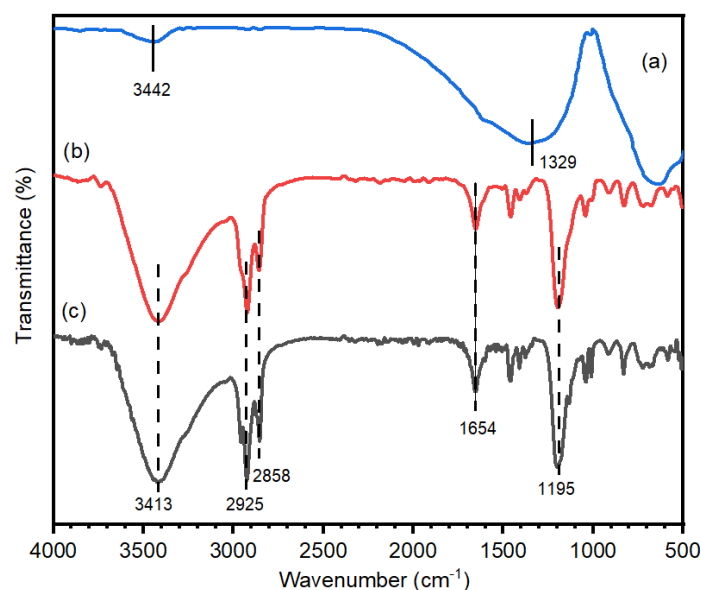


**Fig. 2.** FT-IR spectra of (a) 1-HNO<sub>3</sub>, (b) 3-HNO<sub>3</sub>, (c) 5-HNO<sub>3</sub>

nucleation and stabilizes the metastable anatase phase due to reduced crystallite size (Banfield, 1998).

Further increasing the HNO<sub>3</sub> dosage to 5 mL (Fig. 1c) leads to a more pronounced dominance of anatase peaks, while rutile reflections remain detectable. The calculated phase composition reveals 73.7% anatase and 26.3% rutile, indicating a further shift toward anatase-rich structures. This trend suggests that higher acidity enhances nucleation kinetics, resulting in smaller particle sizes and favoring the stabilization of anatase. At the same time, the persistent presence of rutile implies that the system operates near a phase stability boundary, enabling the formation of an anatase-rutile heterojunction (Scanlon et al., 2013). Therefore, the sample with 62.8% anatase and 37.2% rutile is expected to provide an optimal heterojunction structure, consistent with its superior photocatalytic activity.

The surface chemical structure and bonding characteristics of the synthesized TiO<sub>2</sub> samples were investigated by Fourier-transform infrared (FT-IR) spectroscopy, as shown in Fig. 2. The spectra of all samples exhibit several characteristic absorption bands associated with Ti-O bonding and surface hydroxyl groups.

For the rutile TiO<sub>2</sub> sample (a), a broad absorption band centered around 3400 cm<sup>-1</sup> is observed, which is attributed to the stretching vibration of surface hydroxyl groups (-OH) and adsorbed water molecules. A weak band near 1630 cm<sup>-1</sup> corresponds to the bending vibration of molecular water. In the low wavenumber region (400-800 cm<sup>-1</sup>), a broad and relatively less intense band is detected, which is assigned to Ti-O-Ti lattice vibrations characteristic of the rutile phase (Cargnello et al., 2014; Hsu et al., 2024). The relatively smooth and broad nature of this band reflects the larger crystallite size and lower surface hydroxylation of rutile. For the 3-HNO<sub>3</sub> sample (b) containing 62.8% anatase and 37.2% rutile, the FT-IR spectrum shows a noticeable increase in the intensity of the -OH stretching band (3400 cm<sup>-1</sup>), indicating a higher density of surface hydroxyl groups. This is consistent with the smaller particle size and higher specific surface area observed for anatase-containing samples (Hsu et al., 2024). Additionally, the Ti-O-Ti vibration band in the range of 400-800 cm<sup>-1</sup> becomes more pronounced and slightly broadened, reflecting the coexistence of anatase and rutile phases. The structural heterogeneity arising from the phase junction leads to overlapping vibrational modes, which contribute to the band broadening. For the 5-HNO<sub>3</sub> sample (c) (73.7% anatase and 26.3% rutile), the intensity of

the hydroxyl-related band ( $3400\text{ cm}^{-1}$ ) further increases, indicating enhanced surface hydration and a higher density of active sites. The Ti-O-Ti vibration band becomes stronger and more defined compared to the rutile sample, which is characteristic of anatase-dominated structures with smaller crystallite size (Cargnello et al., 2014). Moreover, slight shifts and increased complexity in the fingerprint region ( $1000\text{--}1500\text{ cm}^{-1}$ ) may be attributed to residual surface species or enhanced surface interactions induced by higher acidity during synthesis.

To further verify the chemical purity and investigate the origin of the observed FT-IR bands at  $2925$  and  $2858\text{ cm}^{-1}$ , elemental analysis was conducted via Energy Dispersive X-ray (EDX) spectroscopy. The EDX spectrum presented in Figure 3 reveals that the catalyst is composed exclusively of Titanium (Ti) and Oxygen (O), with no detectable Carbon (C) content. The quantitative elemental analysis confirms a Ti:O atomic ratio of approximately 1:1.83 (close to the stoichiometric value for  $\text{TiO}_2$ ). These findings effectively rule out the presence of significant bulk organic residues or incomplete hydrolysis products. Consequently, the peaks observed in the FT-IR spectra are attributed to the surface adsorption of atmospheric moisture and minimal surface-bound species, rather than structural carbon contamination that would otherwise interfere with the photocatalytic charge-transfer mechanisms.

The influence of acid on the textural properties and morphological evolution of the  $\text{TiO}_2$  nanostructures was scrutinized using FE-SEM analysis combined with particle size distribution measurements, as depicted in Fig. 4. The micrographs reveal a clear trajectory in particle growth kinetics governed by the  $\text{HNO}_3$  dosage. For the sample synthesized with a limited acid amount (1 mL, Fig. 4a), the material exhibits a coarse morphology characterized by irregular aggregates. The corresponding size distribution histogram (Fig. 4d) confirms a relatively broad dispersion with an average particle diameter ( $d_{\text{mean}}$ ) of approximately 14.1 nm. This quantitative evidence suggests that at low acidity, the reaction is dominated by the uncontrolled condensation of hydrolyzed species. The broad size distribution indicates significant grain growth likely driven by the Ostwald ripening process, where larger particles grow at the expense of smaller ones to reduce surface energy (Cushing et al., 2004)(Fan et al., 2016). In stark contrast, increasing the acid dosage to 3 mL (Fig. 4b) induces a dramatic refinement in the microstructure. The particles transform into highly uniform, discrete nanospheres, and the statistical analysis (Fig. 4e) reveals a sharp reduction in average diameter to 12.0 nm, accompanied by a narrower size distribution. The mechanism underlying this transition can be rationalized by the decisive role of  $\text{H}^+$  ions in

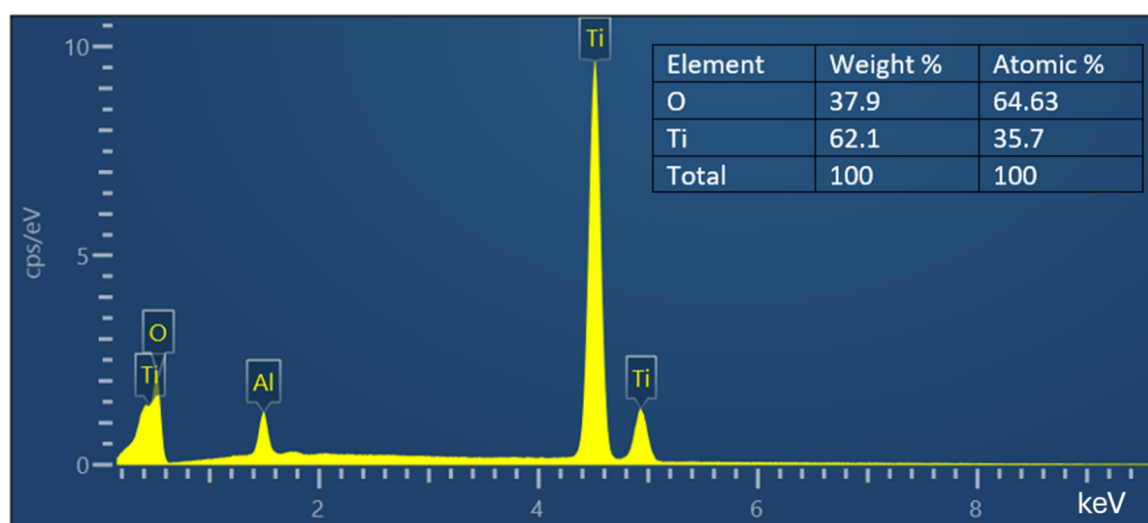


Fig. 3. EDX spectrum and elemental composition of the 3- $\text{HNO}_3$  sample

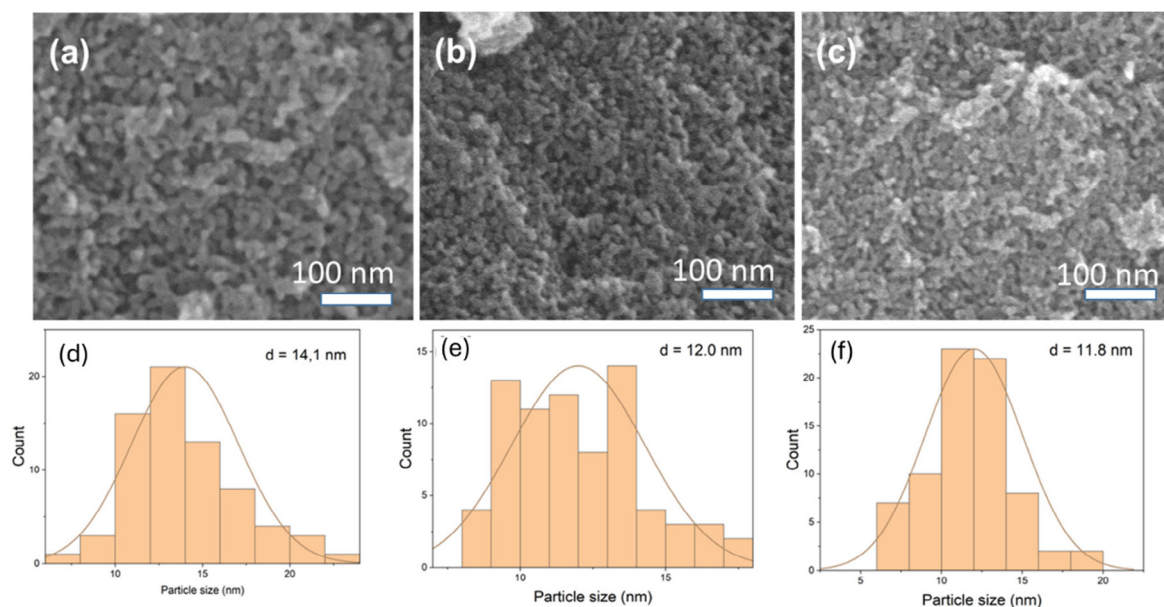


**Fig. 4.** FE-SEM micrographs and corresponding particle size distribution histograms of TiO<sub>2</sub> samples (a,d) 1-HNO<sub>3</sub>, (b,e) 3-HNO<sub>3</sub>, (c,f) 5-HNO<sub>3</sub>

modulating the sol-gel kinetics (Brinker & Scherer, 1990). At this optimal concentration, the accelerated hydrolysis rate triggers a “nucleation burst” consistent with the LaMer mechanism. This generates a high density of nuclei simultaneously, which rapidly consumes the precursor and effectively suppresses the subsequent growth of individual particles, yielding the observed monodispersed nanospheres (Sugimoto, 1987; Victor K et al., 1950). When the acidity is further increased to 5 mL (Fig. 4c), the particle size reduction reaches a saturation plateau, with a measured  $d_{\text{mean}}$  of 11.8 nm (Fig. 4f), which is statistically comparable to the 3 mL sample. However, unlike the well-dispersed 3 mL sample, the 5 mL sample exhibits a degree of interparticle aggregation. This can be attributed to thermodynamic instability: while the primary particle size is confined by the rapid hydrolysis, the excessive ionic strength and high surface energy of these ultra-fine crystallites promote secondary agglomeration to minimize the total surface free energy. Thus, while higher acidity effectively suppresses particle growth, an optimal dosage (3 mL) is required to balance size reduction with morphological dispersity (Hsu et al., 2024).

The formation and phase evolution of TiO<sub>2</sub> nanoparticles in this system can be rationalized based on an acid-mediated sol-gel mechanism coupled with kinetically controlled nucleation and growth processes (Sugimoto et al., 2003). Initially, titanium butoxide undergoes rapid hydrolysis in the presence of water, which is significantly accelerated by the acidic environment provided by HNO<sub>3</sub>. The generated Ti-OH species subsequently undergo condensation to form Ti-O-Ti networks, leading to the formation of amorphous titania nuclei (Sugimoto et al., 2003). The overall reactions can be described as follows:



Importantly, the concentration of H<sup>+</sup> ions plays a decisive role in modulating the nucleation kinetics. At low acid concentrations, the hydrolysis rate is relatively slow, favoring gradual

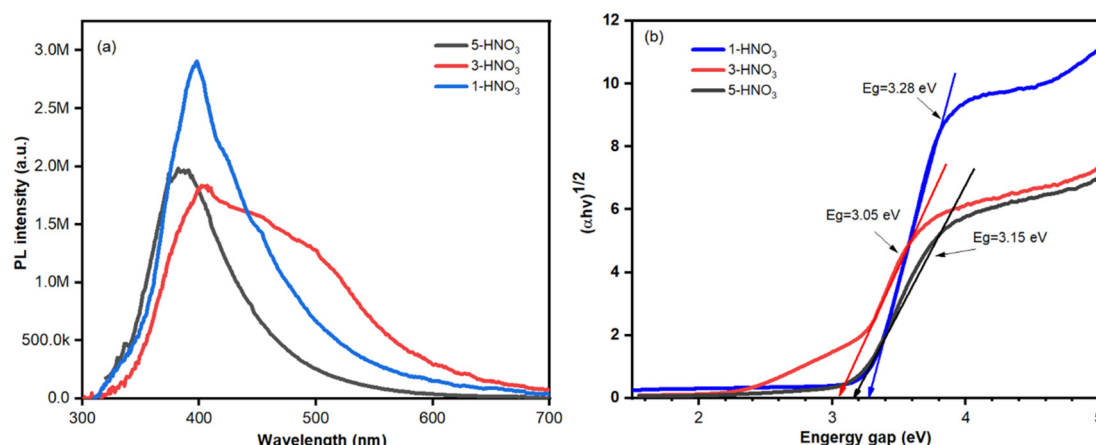


**Fig. 5.** Photoluminescence (PL) spectra (a) and UV–Vis diffuse reflectance spectra with Tauc plots (b) of TiO<sub>2</sub> samples synthesized with different HNO<sub>3</sub> dosages (1, 3, and 5 mL)

nucleation followed by prolonged crystal growth. This condition allows sufficient time for structural rearrangement of TiO<sub>6</sub> octahedra into the thermodynamically stable rutile phase (Hanaor & Sorrell, 2011). In contrast, higher HNO<sub>3</sub> concentrations induce a rapid “nucleation burst,” consistent with the LaMer model, leading to the formation of a large number of ultrafine nuclei within a short time frame (Whitehead et al., 2021; Sugimoto, 1987). The rapid consumption of precursors suppresses subsequent particle growth, resulting in smaller crystallite sizes. According to the size-dependent thermodynamic stability model, anatase becomes more favorable than rutile at nanoscale dimensions due to its lower surface energy (Gribb & Banfield, 1997). Therefore, the reduction in particle size at higher acid concentrations stabilizes the anatase phase, while the coexistence of rutile suggests that the system operates near the phase stability boundary. This leads to the formation of an anatase–rutile heterojunction structure. Such a mixed-phase architecture is highly beneficial for photocatalysis, as the band alignment between anatase and rutile promotes directional charge transfer across the interface, effectively suppressing electron-hole recombination (Scanlon et al., 2013; Schneider et al., 2014). Consequently, the synergistic interplay between phase composition and nanoscale size—both governed by acid-mediated kinetics—accounts for the enhanced photocatalytic performance observed in the optimized samples.

The charge carrier recombination behavior and optical properties of the TiO<sub>2</sub> samples were investigated using photoluminescence (PL) spectroscopy and UV–Vis diffuse reflectance spectroscopy (DRS), as shown in Fig. 5. The PL spectra exhibit a broad emission band centered at 390–420 nm, which is attributed to the radiative recombination of photogenerated electron–hole pairs in TiO<sub>2</sub> (Schneider et al., 2014). Notably, the PL intensity follows the order: 1-HNO<sub>3</sub> > 5-HNO<sub>3</sub> > 3-HNO<sub>3</sub>, in which the 3-HNO<sub>3</sub> sample displays the lowest emission intensity. This indicates a more efficient suppression of charge carrier recombination, which can be associated with the formation of an optimized anatase–rutile heterojunction that facilitates interfacial charge separation (Scanlon et al., 2013; Schneider et al., 2014). In contrast, the pure rutile sample (1-HNO<sub>3</sub>) shows the highest PL intensity, reflecting a higher recombination rate due to the absence of heterojunction interfaces. The 5-HNO<sub>3</sub> sample exhibits intermediate behavior, suggesting that although mixed phases are present, the efficiency of charge separation may be partially affected by factors such as particle aggregation and reduced interfacial contact.

The UV-Vis DRS spectra reveal that all samples exhibit strong absorption in the UV region (<400 nm), characteristic of TiO<sub>2</sub> semiconductors with wide band gaps (M. M. Khan et al., 2014). The optical bandgap energies (E<sub>g</sub>), estimated from Tauc plots, are determined to be

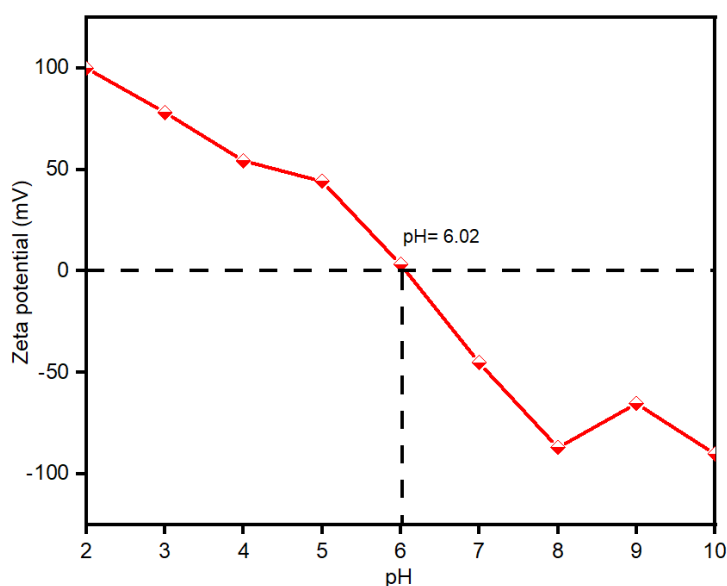


**Fig. 6.** Zeta potential of the 3-HNO<sub>3</sub> TiO<sub>2</sub> nanoparticles as a function of solution pH, showing a point of zero charge (pH<sub>pzc</sub>) at 6.02.

3.28 eV (1-HNO<sub>3</sub>), 3.05 eV (3-HNO<sub>3</sub>), and 3.15 eV (5-HNO<sub>3</sub>). The 3-HNO<sub>3</sub> sample shows a noticeable red shift and the lowest bandgap value, which can be attributed to the synergistic effect of mixed-phase composition and the presence of defect-related states that enhance light absorption (Schneider et al., 2014)(M. M. Khan et al., 2014). Meanwhile, the slightly increased bandgap observed for the 5-HNO<sub>3</sub> sample may be related to its smaller crystallite size, where size-dependent effects and structural variations influence the electronic band structure (H. Zhang & Banfield, 2000a). These results demonstrate that the electronic and optical properties of TiO<sub>2</sub> can be effectively tuned by controlling the acid-mediated synthesis conditions, which modulate both phase composition and particle size.

The mechanism governing this acid-mediated phase selectivity can be rationalized by the interplay between thermodynamic stability and kinetic control during the nucleation process. Bulk Rutile is known to be the thermodynamically stable polymorph of TiO<sub>2</sub>, while Anatase is metastable. Under the low acid condition (1 mL), the slow hydrolysis rate allows sufficient time for the structural rearrangement of the initially formed TiO<sub>6</sub> octahedra into the thermodynamically preferred Rutile configuration (Hanaor & Sorrell, 2011). Conversely, at higher acid concentrations (3-5 mL), the rapid hydrolysis kinetics induce a “nucleation burst,” leading to the formation of ultrafine crystallites with high specific surface area. according to the thermodynamic crossover principle proposed by Zhang and Banfield, Anatase becomes more thermodynamically stable than Rutile when the particle size drops below a critical threshold (typically ~14 nm) due to its lower surface energy (Banfield, 1998). Thus, the high acidity effectively stabilizes the Anatase phase by restricting the particle size. The coexistence of Rutile in these samples suggests that the system operates near the energetic boundary between the two phases, creating a natural heterojunction interface. This mixed-phase architecture is widely recognized to be superior for photocatalysis compared to single-phase counterparts, as the band alignment between Anatase and Rutile facilitates interfacial charge separation and suppresses electron-hole recombination (Scanlon et al., 2013; Ohno et al., 2003).

To better understand the surface properties and their influence on the photocatalytic process, the zeta potential of the optimized 3-HNO<sub>3</sub> photocatalyst was measured across a pH range of 2.0 to 10.0, as shown in Figure 6. The point of zero charge (pH<sub>pzc</sub>) was determined to be 6.02. This result indicates that the surface of the TiO<sub>2</sub> nanoparticles is positively charged at pH <

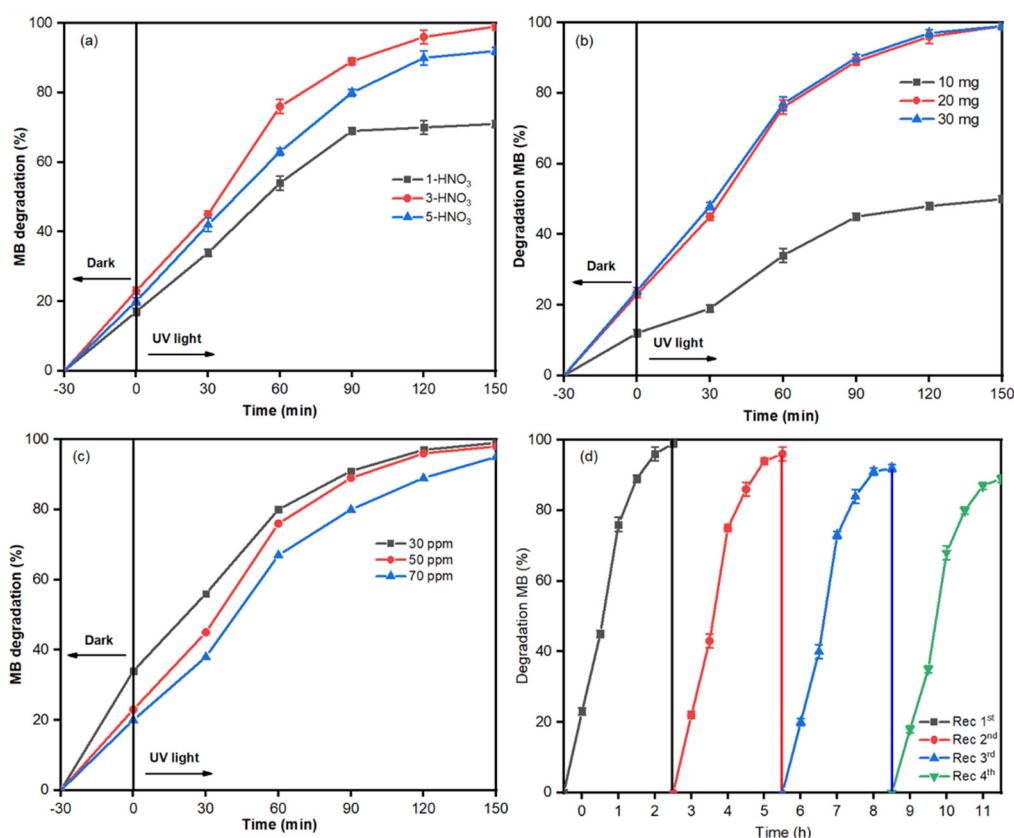


**Fig. 7.** Photocatalytic degradation performance of TiO<sub>2</sub> samples: (a) effect of HNO<sub>3</sub> dosage (1–5 mL); (b) effect of catalyst loading (10–30 mg); (c) effect of initial MB concentration (30–70 ppm); and (d) recyclability over four consecutive cycles under UV irradiation

6.02 and negatively charged at pH > 6.02. Since Methylene Blue (MB) is a cationic dye, its adsorption onto the TiO<sub>2</sub> surface is governed by electrostatic interactions. At pH > 6.02, the negatively charged surface of the TiO<sub>2</sub> facilitates stronger electrostatic attraction toward the cationic MB molecules, thereby enhancing the adsorption efficiency and, consequently, the overall photocatalytic degradation rate. This pH-dependent surface charge property confirms that the electrostatic environment is a critical factor in the synergistic photocatalytic performance observed in this study.

#### *Investigation of photocatalyst activity*

The photocatalytic degradation behavior of Methylene Blue (MB) over the as-prepared TiO<sub>2</sub> samples was systematically evaluated under UV irradiation, as shown in Fig. 7 (a–d). The degradation profiles clearly exhibit two distinct stages, including an initial dark adsorption phase (30 min) followed by a photocatalytic reaction stage under UV illumination. During the dark period, all samples show a noticeable decrease in MB concentration, confirming their adsorption capability. Specifically, the adsorption efficiencies reach approximately 18%, 22%, and 20% for 1-HNO<sub>3</sub>, 3-HNO<sub>3</sub>, and 5-HNO<sub>3</sub>, respectively. The higher adsorption observed for 3-HNO<sub>3</sub> and 5-HNO<sub>3</sub> can be attributed to their smaller particle sizes (12.0 and 11.8 nm) and improved dispersion, leading to a higher specific surface area and more available active sites for dye adsorption.

Upon UV irradiation, the degradation efficiencies increase significantly, and a clear dependence on phase composition is observed in Figure 7(a). After 150 min of irradiation, the

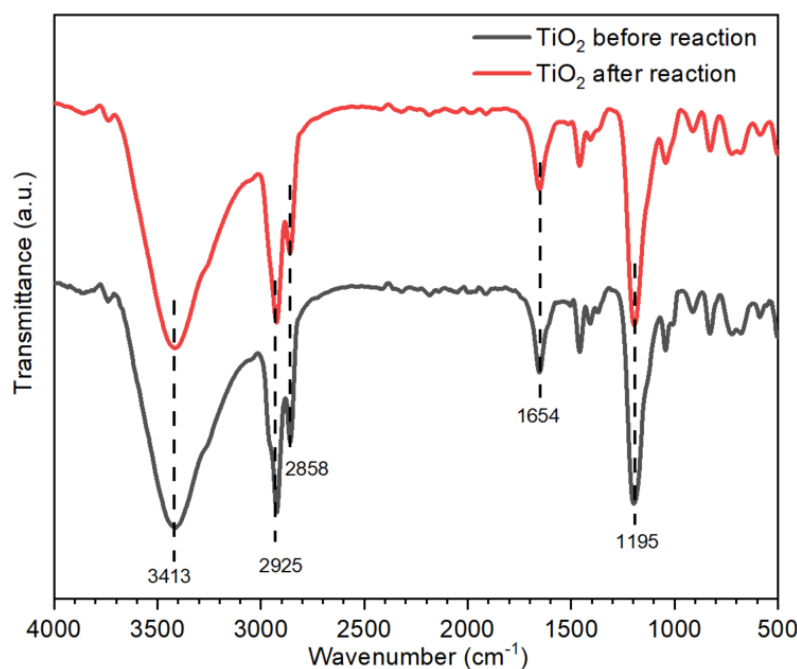


Fig. 8. FT-IR spectra of 3-TiO<sub>2</sub> before and after photocatalytic degradation of MB

degradation efficiencies reach approximately 70%, 99%, and 92% for 1-HNO<sub>3</sub>, 3-HNO<sub>3</sub>, and 5-HNO<sub>3</sub>, respectively. The pure rutile sample (1-HNO<sub>3</sub>) exhibits the lowest activity, which is consistent with its high PL intensity, indicating rapid electron–hole recombination. In contrast, the mixed-phase samples demonstrate markedly enhanced performance due to the formation of anatase–rutile heterojunctions. Among them, the 3-HNO<sub>3</sub> sample shows the highest degradation efficiency, which can be correlated with its optimal phase composition (62.8% anatase / 37.2% rutile), lowest recombination rate, and reduced bandgap (3.05 eV). Although the 5-HNO<sub>3</sub> sample contains a higher anatase fraction (73.7%), its degradation efficiency is slightly lower, suggesting that excessive anatase content and particle aggregation may reduce the effective heterojunction interface and limit charge transfer efficiency.

The effect of catalyst dosage was further evaluated by varying the amount from 10 to 30 mg (Fig. 7b). At 60 min, the degradation efficiencies are approximately 34%, 75%, and 78% for 10 mg, 20 mg, and 30 mg, respectively, indicating a significant improvement with increasing catalyst loading. However, after 150 min, both 20 mg and 30 mg samples achieve nearly complete degradation (~99%), while the 10 mg sample reaches only ~50%. The negligible difference between 20 mg and 30 mg at longer irradiation times suggests the occurrence of a light shielding effect at higher catalyst concentrations, which limits further enhancement in photocatalytic efficiency.

The influence of initial MB concentration was also investigated (Fig. 7c). At 150 min, the degradation efficiencies are approximately 99%, 97%, and 95% for initial concentrations of 30, 50, and 70 ppm, respectively. The decrease in efficiency with increasing concentration can be attributed to reduced light penetration and increased competition for active sites, which limit the generation and utilization of reactive oxygen species.

Finally, the reusability of the photocatalyst was examined over four consecutive cycles (Fig. 7d). The degradation efficiency remains above 95% in the first three cycles and slightly decreases to approximately 90% in the fourth cycle, indicating good stability and recyclability. The minor decline in performance may be due to partial surface fouling or material loss during the recovery process. These results demonstrate that the photocatalytic performance is strongly governed by

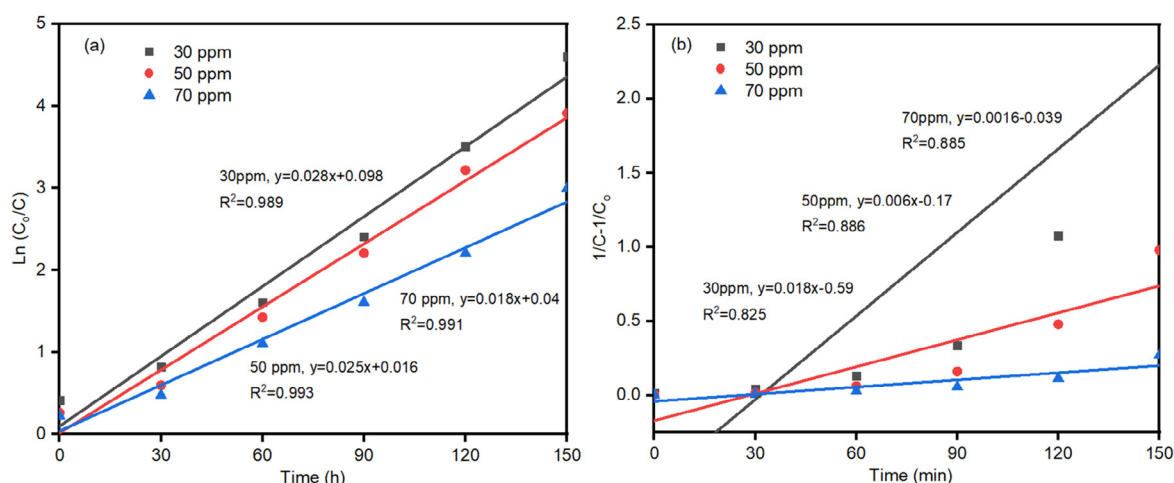


**Fig. 9.** Kinetic analysis of Methylene Blue (MB) degradation over TiO<sub>2</sub> photocatalysts at different initial concentrations: (a) pseudo-first-order kinetic plots ( $\ln(C_0/C)$  vs. time) and (b) pseudo-second-order kinetic plots ( $1/C - 1/C_0$  vs. time).

the synergistic interplay between phase composition, particle size, and surface properties, with the optimized anatase-rutile ratio (3-HNO<sub>3</sub> sample) providing the most favorable balance for efficient charge separation and surface reaction processes.

To evaluate the stability and reusability of the 3-TiO<sub>2</sub> catalyst, its chemical bonding characteristics after four reaction cycles were investigated using FT-IR spectroscopy. As shown in Figure 8, the FT-IR spectra of the catalyst before and after the reaction exhibit almost identical features. The characteristic peaks at 3413 cm<sup>-1</sup> (attributed to O-H stretching vibrations), 2925 and 2858 cm<sup>-1</sup> (C-H stretching), 1654 cm<sup>-1</sup> (O-H bending), and 1195 cm<sup>-1</sup> confirm the persistence of surface hydroxyl groups and the structural integrity of the catalyst. The lack of significant shifts or disappearance of these peaks indicates that the 3-TiO<sub>2</sub> catalyst possesses excellent chemical stability and structural robustness under the experimental conditions, ensuring its potential for repeated use in wastewater treatment applications.

To evaluate the degradation kinetics of Methylene Blue (MB) of the TiO<sub>2</sub> photocatalysts, the experimental data were fitted using both pseudo-first-order and pseudo-second-order kinetic models, as illustrated in Fig. 9(a,b).

The pseudo-first-order model, expressed as  $\ln(C_0/C) = kt$ , exhibits excellent linear correlations for all investigated concentrations (30, 50, and 70 ppm), with high determination coefficients ( $R^2 = 0.989, 0.993$ , and  $0.991$ , respectively). The corresponding apparent rate constants ( $k$ ) were determined to be 0.028, 0.025, and 0.018 min<sup>-1</sup> for 30, 50, and 70 ppm, respectively. The slight decrease in  $k$  with increasing initial concentration indicates that higher dye concentrations hinder the degradation rate, likely due to reduced light penetration and increased competition for active sites on the catalyst surface (Chen et al., 2020).

In contrast, the pseudo-second-order model ( $1/C - 1/C_0 = kt$ ) shows significantly poorer linear fitting, with lower  $R^2$  values ranging from 0.825 to 0.886. This deviation suggests that the degradation process is not governed by second-order adsorption-controlled kinetics, but rather dominated by surface reaction processes involving photogenerated reactive species (Ho & McKay, 1999).

The superior fitting of the pseudo-first-order model confirms that the photocatalytic degradation of MB follows Langmuir-Hinshelwood (L-H) kinetics, where the reaction rate depends on the adsorption equilibrium and surface reaction between adsorbed species and reactive oxygen species (ROS) (Henderson, 2011; Schneider et al., 2014). Under dilute conditions, this model simplifies to apparent first-order kinetics, which is consistent with the observed linear

**Table 1.** Comparison of photocatalytic degradation rate constants (k) of TiO<sub>2</sub>-based catalysts for methylene blue (MB) degradation under UV or UV/Vis irradiation

| Catalyst                     | Method       | k (min <sup>-1</sup> ) | Condition | Ref                           |
|------------------------------|--------------|------------------------|-----------|-------------------------------|
| TiO <sub>2</sub> (this work) | Hydrothermal | 0.028                  | UV, MB    | This work                     |
| Degussa P25                  | Commercial   | 0.010-0.020            | UV, MB    | (Hurum et al., 2003)          |
| TiO <sub>2</sub> (sol-gel)   | Sol-gel      | 0.012-0.025            | UV, MB    | (Reyes-Coronado et al., 2008) |
| N-doped TiO <sub>2</sub>     | Doping       | 0.030-0.045            | UV/Vis    | (Asahi et al., 2001)          |

relationships. Furthermore, the decrease in rate constant with increasing initial concentration can be attributed to: (i) attenuation of UV light due to increased solution opacity, (ii) saturation of active sites on the catalyst surface, and (iii) competitive consumption of reactive radicals (Linsebigler et al., 1995). These factors collectively limit the effective interaction between MB molecules and photogenerated charge carriers.

To further evaluate the photocatalytic performance of the as-prepared TiO<sub>2</sub> samples, the apparent rate constants (k) obtained in this study were compared with previously reported TiO<sub>2</sub>-based photocatalysts for Methylene Blue degradation. As summarized in Table 1, the rate constant of the 3-HNO<sub>3</sub> sample, which yielded the highest photocatalytic activity (k = 0.028 min<sup>-1</sup>) is comparable to or higher than many reported systems under similar UV irradiation conditions.

For instance, commercial Degussa P25, a widely used benchmark photocatalyst composed of mixed anatase-rutile phases (~80/20), typically exhibits rate constants in the range of 0.010-0.020 min<sup>-1</sup> under comparable experimental conditions (Hurum et al., 2003; Schneider et al., 2014). Similarly, sol-gel-derived TiO<sub>2</sub> nanoparticles often exhibit k values ranging from 0.012 to 0.025 min<sup>-1</sup>, depending on particle size and crystallinity (Reyes-Coronado et al., 2008). More advanced systems, such as doped or composite TiO<sub>2</sub> materials, can achieve higher rate constants (0.030-0.050 min<sup>-1</sup>), but usually require more complex synthesis routes or additional modification steps (Asahi et al., 2001). The relatively high rate constant achieved in this work, despite the use of a simple one-step hydrothermal method, highlights the effectiveness of phase engineering as a strategy to enhance photocatalytic activity. In particular, the optimized anatase-rutile ratio (62.8/37.2) provides an efficient heterojunction interface that facilitates charge separation, leading to improved reaction kinetics without the need for doping or noble metal loading.

The photocatalytic efficiency is primarily governed by the anatase-rutile heterojunction formed during acid-mediated nucleation. As the acidity increases, the preferential dissolution-recrystallization process facilitates the formation of this heterojunction, which acts as a built-in potential gradient to separate charge carriers. By tuning the HNO<sub>3</sub> concentration, we effectively modulate the phase ratio and particle size, creating an architecture that optimizes both the active surface area and the vectorial charge transfer. This unified mechanism explains the observed catalytic performance, avoiding redundant characterizations of phase evolution at different acidic stages. Upon UV excitation, photons with energy exceeding the bandgap ( $E \geq E_g$ ) generate electron-hole pairs ( $e^-/h^+$ ) within the TiO<sub>2</sub> lattice. In a single-phase system, these carriers suffer from rapid bulk recombination; however, in the optimized 3 mL sample, the staggered band alignment between the Anatase and Rutile polymorphs constructs a built-in potential gradient (Scanlon et al., 2013; Schneider et al., 2014). This energetic architecture acts as a directional driving force, facilitating the vectorial transfer of photo-excited electrons and holes across the phase junction, thereby extending their lifetime significantly (Low et al., 2017). Once separated, the charge carriers migrate to the catalyst surface to trigger the redox cascade. The thermodynamic potential of the conduction band electrons is sufficiently negative to reduce adsorbed oxygen molecules (O<sub>2</sub>), yielding superoxide anion radicals ( $\cdot O_2^-$ ). Concurrently, the

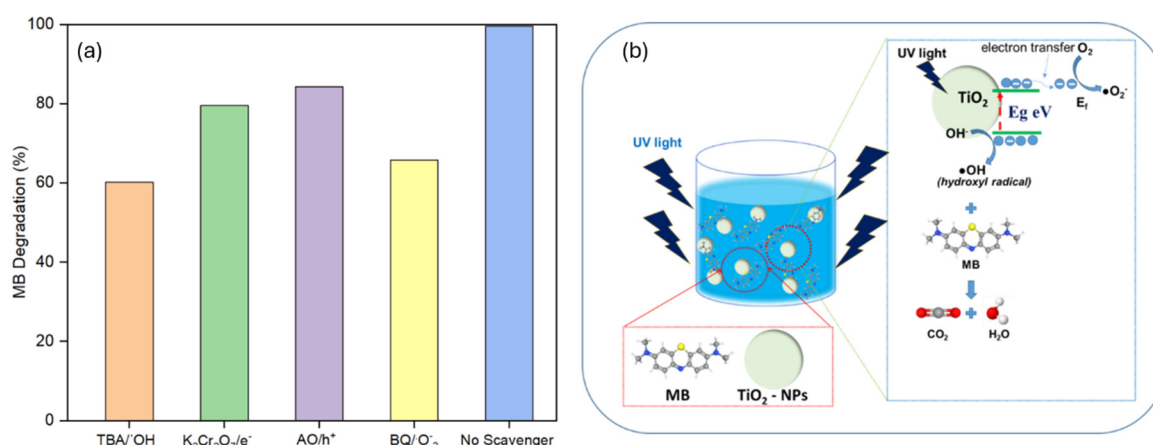
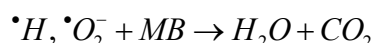
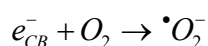
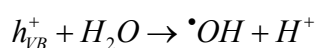
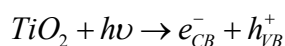


**Fig. 10.** (a) The active species trapping experiments for the degradation of MB over the 3-TiO<sub>2</sub> photocatalyst, (b) Mechanism of MB degradation by TiO<sub>2</sub> under UV irradiation.

valence band holes, possessing a strong oxidative potential, react with surface-bound water or hydroxyl groups to generate hydroxyl radicals ( $\bullet OH$ ) (Chen et al., 2020). To systematically determine the role of each reactive species in the degradation process, scavenger experiments were conducted using Tert-butanol (TBA) for  $\bullet OH$ , potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) for e<sup>-</sup>, ammonium oxalate (AO) for h<sup>+</sup>, and p-benzoquinone (BQ) for  $\bullet O_2^-$  (Fig. 10a). As illustrated in Fig. 10a, the degradation efficiency of MB drops significantly upon the addition of TBA, reaching the lowest value (60.2%), which confirms that  $\bullet OH$  radicals are the primary active species responsible for the degradation of MB. The addition of BQ also causes a considerable decrease in efficiency (65.8%), indicating that  $\bullet O_2^-$  radicals play a vital supplementary role. Conversely, the smaller decrease observed with AO and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> suggests that h<sup>+</sup> and e<sup>-</sup> contribute to a lesser extent. These results provide direct experimental evidence for the proposed mechanism where  $\bullet OH$  serves as the dominant oxidant. Based on the literature regarding the photodegradation of MB, the process involves the following sequence: (1) Demethylation: The initial stage involves the step-wise removal of methyl groups from the MB molecule, leading to the formation of Azure A, Azure B, and Azure C as primary intermediate products (Houas et al., 2001); (2) Ring opening: The thiazine ring and aromatic structures are subsequently attacked by  $\bullet OH$  radicals, leading to ring-opening reactions that produce smaller organic molecules such as carboxylic acids, NH<sub>4</sub>, NO<sub>3</sub>, and eventually CO<sub>2</sub> and H<sub>2</sub>O. This step-wise degradation ensures the complete mineralization of the dye. The entire photocatalytic pathway is governed by the following reactions (Laghrib et al., 2025):



Ultimately, the heterojunction-induced charge separation serves as the kinetic rate-determining step, ensuring that a maximized flux of ROS is available to degrade the organic pollutants efficiently.

## CONCLUSION

In this study, TiO<sub>2</sub> nanoparticles with tunable phase composition were synthesized via a facile hydrothermal route by controlling HNO<sub>3</sub> dosage. The results demonstrate that acidity critically governs nucleation kinetics, particle size, and the anatase–rutile phase balance. An optimized mixed-phase structure (62.8% anatase/37.2% rutile) was achieved at 3 mL HNO<sub>3</sub>, exhibiting reduced particle size (12 nm), suppressed charge recombination, and a narrowed bandgap (3.05 eV). Consequently, this sample delivered the highest photocatalytic efficiency (99.5% MB degradation) and a superior kinetic rate constant (0.028 min<sup>−1</sup>). The enhanced performance is primarily attributed to efficient charge separation at the anatase-rutile heterojunction combined with increased surface reactivity. These findings highlight phase engineering via acid-mediated synthesis as a simple and effective strategy for designing high-performance TiO<sub>2</sub> photocatalysts for environmental remediation.

## GRANT SUPPORT DETAILS

The present research has been financially supported by the key research project No. ĐTTĐ2425–35, University of Transport Technology.

## CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

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