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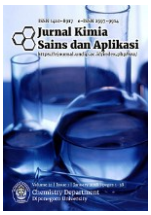

Two-Stage Hydrothermal Synthesis of TiO_2 Nanotubes with Variation of Precursor Type for Diazinon Photodegradation

Tanti Haryati [1,*], Mustafid A'yun Assiddiq [1], Suwardiyanto [1], Novita Andarini [1], Yudi Aris Sulistiyo [1]

[1] Department of Chemistry, Faculty of Mathematics and Natural Science, University of Jember, Jember 68121, Indonesia

* Corresponding author: tanti@unej.ac.id

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Abstract

TiO_2 is commonly used as a photocatalyst for the photodegradation of harmful chemical compounds, such as diazinon. Its photocatalytic properties can be enhanced by fabricating it into nanotubes. TiO_2 nanotube (TNTs) has a large surface area with good photon absorption and electron transport. This study aims to determine the effect of precursor type on the morphology, crystal structure, and photocatalytic activity of the resulting TNTs against diazinon. TNTs synthesis was carried out through a two-stage hydrothermal method using TiO_2 micro powder precursors in anatase and rutile phases. The photocatalytic activity of TNTs was tested against diazinon photodegradation. The morphology of TNTs resulting from the first and second hydrothermal processes was fiber-shaped for anatase TNP precursor (TNPa) and rutile TNP precursor (TNPr). TEM characterization showed that the TNT particles were tubular with an outer diameter of 2.27-10.92 nm and an inner diameter of 1.10-4.2 nm. Some impurities, such as sodium titanate and hydrogen titanate, still appear in the diffraction patterns of TNTa and TNTr. The TNTr photocatalyst underwent crystal phase transformation into anatase, which was compared with the JCPDS data. The percentage of degradation for TNTa photocatalyst is slightly greater than TNTr, reaching 85.9% and 82.4%, respectively.

1. Introduction

Titanium dioxide (TiO_2) is a semiconductor widely employed as a photocatalyst product. TiO_2 has three distinct crystal phases: anatase, rutile, and brookite [1]. TiO_2 anatase exhibits the most pronounced photocatalytic activity of the crystal types, attributable to its relatively low charge carrier recombination rate. The photocatalytic activity of TiO_2 can be enhanced by modifying its morphology to a nanoscale, with a variety of morphologies such as nanofibers, nanorods, and nanotubes [2]. Photocatalyst products with tube morphology have been observed to exhibit greater photocatalytic activity than other nanoscale morphologies [3].

The synthesis of TiO_2 nanotubes (TNTs) can be achieved through a crystal growth process utilizing the hydrothermal method. The hydrothermal method employed comprises two stages. Lorturn *et al.* [4] have demonstrated that the utilization of a two-stage hydrothermal process can enhance the surface area of TiO_2 with nanotube morphology. The hydrothermal process is conducted within a closed system, characterized by elevated temperatures and pressures, and involves the utilization of solvent compounds, commonly referred to as "mineralizers", such as sodium hydroxide (NaOH). The morphology of TNTs produced via the hydrothermal process can be influenced by several factors, including the type of precursor, temperature, reaction time, alkali concentration, and the ratio of TiO_2 to NaOH [5]. The differences in the crystal structure of TiO_2 can result in variations in band gap energy values, which in turn influence the type of light absorbed. For instance, the band gap energy of anatase TiO_2 is 3.2 eV, while that of rutile TiO_2 is 3.0 eV [6].

The photocatalytic activity of TNTs in degrading organic compounds depends on the interaction between

photon energy and the TiO_2 semiconductor, which leads to the generation of electron–hole pairs. The holes formed react with water molecules to produce hydroxyl radicals (·OH), which can break the chemical bonds in organic compounds such as diazinon [7]. Zulfiqar *et al.* [8] reported the photocatalytic activity of TNTs on organic compounds like methyl orange, achieving a degradation rate of 95.55%.

This study synthesized TNTs using a two-stage hydrothermal method with a variety of precursor types: rutile and anatase crystal structures. The crystal structure and morphology of each stage of synthesis were observed to identify any changes that occurred and to assess the photocatalyst activity of the resulting material in the degradation of diazinon.

2. Experimental

TNTs synthesis was conducted using a two-stage hydrothermal method. In the initial stage, TiO_2 micropowder was employed as the precursor, while the resulting product from the first stage was utilized as the precursor in the subsequent stage [9].

2.1. Materials

The following materials were used in this experiment: TiO_2 micropowder (anatase and rutile, Merck), NaOH (Merck), NaH_2PO_4 (Merck), Na_2HPO_4 (Merck), HCl 37% (Merck), distilled water, aluminum foil, commercial diazinon 600 EC (PT. Petrokimia Kayaku), universal pH indicator, and Whatman 42 filter paper.

2.2. Initial Synthesis Stage: Formation of Titanium Dioxide Nanoparticles (TNPs)

In the initial stage of the process, 0.678 g of anatase micropowder (TiO_2 precursor) was dissolved in 85 mL of 10 M NaOH solution. The mixture was agitated for 30 minutes with a stirrer and then transferred to a 100 mL autoclave. The autoclave was placed in an oven set to a temperature of 130°C and left to stand for 24 hours. The autoclave was then permitted to stand for four hours at room temperature. The resulting solid was transferred to a glass beaker and washed with 0.1 M HCl under continuous stirring until the pH reached 7. The solid was then separated using Whatman 42 filter paper and dried in an oven at 80°C for 12 hours. The same procedure was used to prepare the TiO_2 precursor from rutile. The expected product was TiO_2 nanoparticles (TNPs). Products synthesized from anatase precursors are referred to as TNPs(a), while those from rutile precursors are referred to as TNPs(r).

2.3. Second-stage Synthesis of TiO_2 Nanotubes (TNTs)

The second stage of the synthesis of TNTs involved using 1.356 g of TNPs(a), dissolved with 10 M NaOH, in a volume of up to 85 mL. The synthesis procedure followed the same steps as those used for TNPs(a), with the exception of the washing process. In this stage, the solid was washed with 1 M HCl until the pH reached 3, followed by rinsing with distilled water until a neutral pH of 7 was achieved. The resulting solids were then separated using Whatman No. 42 filter paper and dried in an oven at 80°C for 12 hours. The same procedure was applied for the preparation of TNTs(r) from TNPs(r). The anticipated outcome was TNTs. Products synthesized from TNPs(a) and TNPs(r) are referred to as TNTs(a) and TNTs(r), respectively. The differences in the synthesis treatments used in the first and second stages are outlined in Table 1.

2.4. Characterizations

Morphological characterization was conducted using scanning electron microscopy (SEM, JEOL JSM-IT 200) with a maximum magnification of 40,000×, and particle size distribution analysis was performed using ImageJ Software. The diffraction patterns were characterized using X-ray diffraction (XRD) with a PANalytical Xpert MPD diffractometer, operated over a 2θ range of 5–60°. Crystalline structure was examined through X-ray diffraction (XRD) using a PANalytical X'Pert MPD diffractometer, operated at a scanning range of 2θ = 5–60°. The tubular morphology of the TNT samples was further observed using transmission electron microscopy (TEM, JEM-1400), with magnification up to 1,500,000×. The tube diameters were measured using ImageJ software. The band gap energy was determined using UV- Vis diffuse reflectance spectroscopy (UV-Vis DRS) in the wavelength range of 200–800 nm. The absorbance data were analyzed using the Tauc plot method, as shown in Equation 1.

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g) \quad (1)$$

Where, α is the absorption coefficient, h is Planck's constant, ν is the vibration frequency, A is a proportionality constant, n is the nature of the TiO_2 sample transition, and E_g is the band gap energy.

2.5. Photocatalytic Activity Test

The photocatalytic activity of TNTs on diazinon compounds was investigated in a photocatalytic reactor equipped with a 40 W ultraviolet lamp (Philips Stick). A solution of 25 ppm diazinon (up to 20 mL) and TNT (up to 50 mg) was prepared in a 50 mL glass beaker. The irradiation process was conducted at room temperature (25°C) and at a neutral pH of 7. The glass beaker containing the mixture was placed in the photoreactor. The degradation process was conducted with constant stirring (300 rpm) and irradiation durations of 30, 120, and 210 minutes. Subsequently, the photodegradation results were centrifuged at 3000 rpm for 30 minutes and then allowed to stand until two distinct phases formed. The solution was subsequently filtered using filter paper to separate the filtrate from the residue. The filtrate was analyzed using a UV-Vis spectrophotometer, with absorbance measurements recorded over a wavelength range of 200–400 nm.

Table 1. Variation of TNPs and TNTs synthesis treatment

Variation	TiO_2 anatase	TiO_2 rutile	TNPs(a)	TNPs(r)
Mole ratio of TiO_2/NaOH	0.01:1	0.01:1	0.02:1	0.02:1
Acid washing	0.1 M, pH 7	0.1 M, pH 7	1 M, pH 3	1 M, pH 3

2.6. Analysis of Photodegradation Results

The photodegradation concentration results were analyzed using the calibration curve equation data with a 1 to 25 ppm diazinon standard solution. The highest absorbance value determines the maximum wavelength of the diazinon solution. The concentration of the photodegradation process can be calculated with the line equation, y = mx + c, where x represents the final concentration of photodegradation (C_t) obtained in Equation 2.

$$C_t = \frac{y - c}{m} \quad (2)$$

Equation 3 can be used to determine the proportion of TNTs' capacity to degrade diazinon (%R).

$$R(\%) = \left(\frac{C_0 - C_t}{C_0}\right) \quad (3)$$

3. Results and Discussion

3.1. Morphology and Particle Size

Morphology and particle size were analyzed using SEM micrographs. The precursor samples have a spherical morphology, with average particle sizes of 175.03 nm for anatase TiO_2 and 225.30 nm for rutile TiO_2, as shown in Figure 1(a–b). Following the first stage of hydrothermal synthesis, a morphological transformation occurred, resulting in the formation of fibrous structures, as illustrated in Figure 1(c-d). During this stage, the Ti–O–Ti bonds in the precursor were broken upon the addition of NaOH solution, leading to the formation of sodium titanate ($Na_2Ti_3O_7$).

This transformation is attributed to the role of NaOH as an excess mineralizer, which induces surface tension, causing the sodium titanate sheet layers to roll and form a fibrous morphology. The results of the synthesis of the precursors are then called TiO_2 nano particles anatase TNPs(a) for anatase precursors and TiO_2 nano particles rutile TNPs(r) for rutile precursors. The first stage of the hydrothermal method synthesis produced an average particle size of 39.89 nm and 32.51 nm for TNPs(a) and TNPs(r), respectively, as shown in Figure 1(c-d).

The second stage of synthesis, utilizing the precursor from the initial stage, as illustrated in Figure 2(a-b), demonstrates that the morphology remains fiber-shaped, as expected. This morphology is anticipated to transition to a tubular nanostructure, referred to as TNTs. The average particle size of the TNTs(a) and TNTs(r) samples was measured to be 27.48 nm and 32.52 nm, respectively. Further observations were conducted to obtain the tubular morphology in the second stage of synthesis using TEM characterization.

Figure 3 depicts micrographs of the TNTs(a) and TNTs(r) samples, which exhibited well-defined tubular structures. The outer and inner diameters of TNTs(a) ranged from 3.93–11.43 nm and 2.50–4.25 nm, respectively, while those of TNTs(r) ranged from 2.27–10.92 nm and 1.10–4.26 nm, respectively. A similar two-stage synthesis approach was previously reported by Bayan *et al.* [10], resulting in the formation of TNTs with diameters in the range of 5–8 nm.

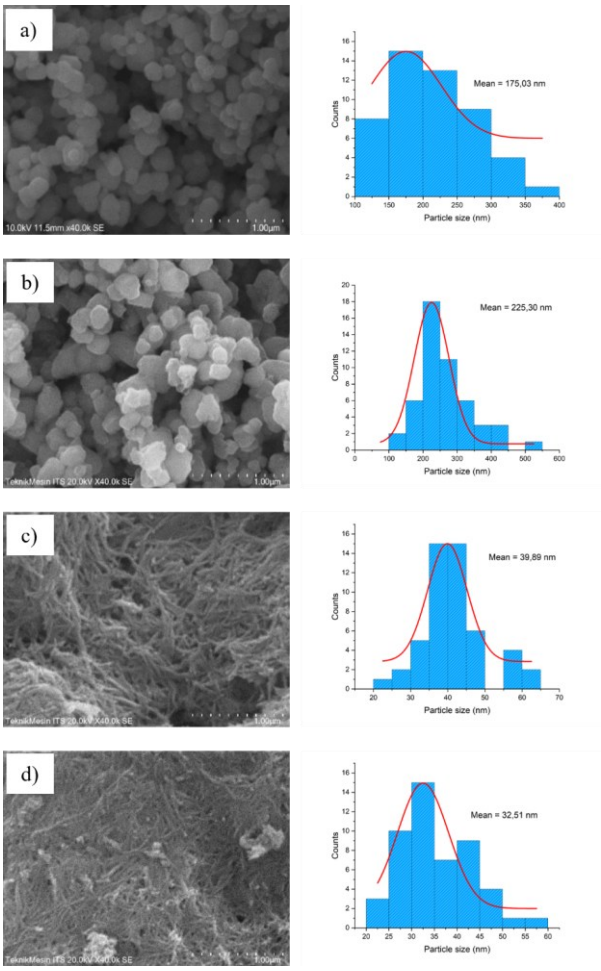

Figure 1. SEM images and particle size distribution of (a) anatase TiO_2 precursor, (b) rutile TiO_2 precursor, (c) TNPs(a), and (d) TNPs(r)

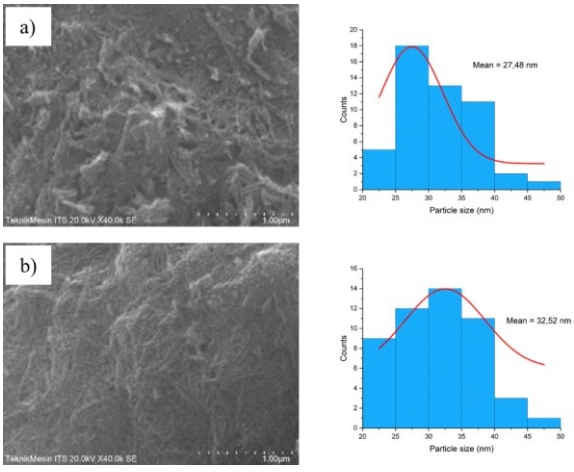

Figure 2. SEM images and particle size distributions of (a) TNTs(a) and (b) TNTs(r)

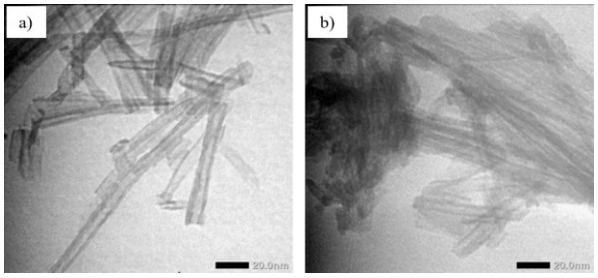

Figure 3. TEM images of (a) TNTs(a) and (b) TNTs(r)

3.2. Crystalline Phase

The crystal phase of each precursor and sample was characterized using XRD. Figure 4 depicts the complete set of diffraction patterns for the samples, as classified according to the Joint Committee on Powder Diffraction Standards (JCPDS), in the bottom row (1–4). The precursors exhibited both rutile and anatase phases. The TNPs(a) sample displayed an anatase phase at 2θ = 48.35°, while the TNPs(r) sample showed a mixed rutile–anatase phase at 2θ = 27.56°, 36.19°, 41.34°, 48.34°, 54°, 41°, and 56.72°. Impurity phases such as sodium titanate (NT) and hydrogen titanate (HT) were also identified. The formation of NT is attributed to the reaction between TiO_2 and NaOH without subsequent ion exchange in HCl, while HT forms without H^+ ion release during heating. The persistence of the rutile phase in TNPs(r) may result from a larger particle size, which requires higher heating pressure and longer processing time to achieve complete transformation.

The diffraction patterns of the TNTs(a) and TNTs(r) samples indicate the presence of the anatase phase at 2θ = 48.25° and 48.44°, respectively. In the rutile precursor, a transformation process occurs whereby the initial synthesis phase results in a mixed phase, which subsequently transforms into the anatase phase. This transformation is a consequence of the synthesis process, which employs a lower temperature to facilitate the conversion of rutile to anatase. Anatase structures are formed at lower temperatures than rutile, specifically between 200 and 500°C, according to the principles of thermodynamics [11]. However, the TNTs(a) and TNTs(r) samples also exhibit the presence of NT and HT impurities, which contribute to the observed low crystallinity.

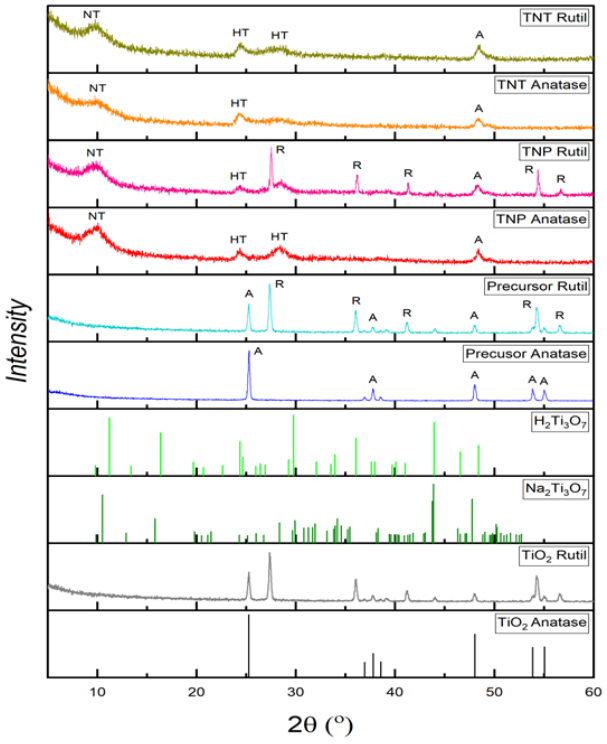

Figure 4. XRD diffractogram of TNTs (A = anatase, R = rutile, NT = sodium titanate, HT = hydrogen titanate)

3.3. Band Gap Energy

The band gap energy value (E_g) is determined by entering the absorbance of UV-Vis DRS measurements into the Tauc plot equation. The transition value (n) for TiO_2 anatase is n = 2, as the transition occurs directly. Figure 5 illustrates the E_g value for the TNTs(a) and TNTs(r) samples. The E_g values obtained for the TNTs(a) and TNTs(r) samples are 3.21 eV and 3.15 eV, respectively. The TNTs(a) sample exhibits a slightly higher energy value than the TNTs(r) sample. The observed decrease in band gap energy value in the TNTs(r) sample can be attributed to the presence of elevated levels of impurities, which reduce the absorption capacity of TNTs products to ultraviolet light sources and impede the recombination of electron-hole pairs in the photocatalytic process.

3.4. Photocatalysis of TNT

The determination of the percent degradation value of diazinon is illustrated in Figure 6, which depicts the relationship between the length of irradiation time and the percent degradation value. The photocatalytic process was performed under ultraviolet light for up to 210 minutes, with samples collected at 30, 120, and 210 minutes. The analysis demonstrated that the TNTs(a) sample exhibited a higher percent degradation value of diazinon at 210 minutes of irradiation, reaching 85.9%, compared to 82.4% for the TNTs(r) sample

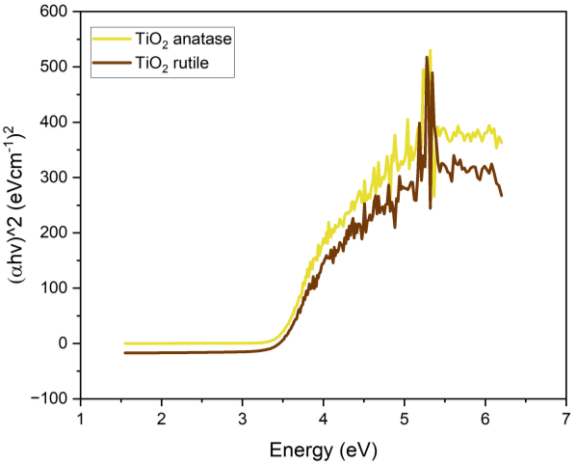

Figure 5. Tauc plot of TNTs versus photon energy

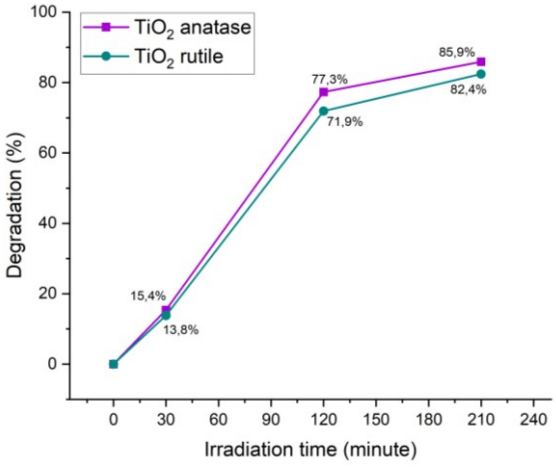

Figure 6. Graph of percent degradation of diazinon versus irradiation time

Kalantary *et al.* [12] reported that the photocatalytic process utilizing TiO_2 nanoparticles of the anatase phase can achieve a percent degradation of diazinon up to 99.98% under UV irradiation at a wavelength of 125 nm for 120 minutes. The results of the photocatalysis process are affected by several factors, including differences in composition and concentration between the catalyst and the diazinon solution used. As shown in Figure 6, the degradation percentage increased with longer irradiation time, indicating a consistent decrease in diazinon concentration. It is evident that other factors, such as the smaller particle size of the TNT photocatalyst, result in a larger surface area. The outcome of this process is an enhancement in the capacity of TNT(a) photocatalyst to absorb photons, thereby leading to an augmentation in the production of ·OH. It has been demonstrated that the effectiveness of diazinon photodegradation is greater than that of TNT(r), with the former achieving 85.9% and the latter reaching 82.4%.

4. Conclusion

This study demonstrated the synthesis of TiO_2 nanotubes (TNTs) via a two-stage hydrothermal method. Both anatase and rutile phase TiO_2 precursors yielded TNT photocatalysts with anatase crystalline structures. The photocatalytic degradation of diazinon under UV irradiation for 210 minutes reached 85.9% for TNTs(a) and 82.4% for TNTs(r), indicating effective photocatalytic performance, particularly from the anatase-derived nanotubes.

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