

## Conference Paper

# Synthesis and Characterization of TNTs/Polyaniline Composite as Photocatalyst Degradation of Rhodamin B by Visible Light

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## Abstract

The purpose of this research is to study the effect of the amount of aniline on their photocatalytic activity. Nano TiO<sub>2</sub> was synthesized using sol-gel method with TiPP precursor. XRD characterization results showed that nano TiO<sub>2</sub> with calcination temperature of 450 °C had size of 13.8 nm with high crystalline. The diffraction peaks of nano TiO<sub>2</sub> at 2θ are 24.45°; 37.075°; 47.26° and 53.18°. Nano TiO<sub>2</sub> was then synthesized with hydrothermal treatment 24 h of 140 °C to produce TNTs. The results of XRD analysis shows anatase phase with field (004) and (200). The morphology of TNTs begins to form at the calcinations temperature of 600 °C with textural coefficient value of 0.998 3 . Synthesis of composite TNTs/PANI (polyaniline) was done by in situ polymerization technique of aniline which was already contained nano TiO<sub>2</sub>. The molar ratio of aniline and APS in the synthesis of a composite is 1:1.5 with the addition of aniline of 15 %; 20 % and 25 % (w/w %). Characterization using FTIR showed the stretching vibration of the C=N in wavelength of 1 600 cm<sup>-1</sup> to mark the formation of quinonoid compounds of polyaniline. The test of the rhodamine B degradation gave the best results on the 25 % TNTs/PANI composite, with the degradation percentage of 58.73 %. The characterization results using dr-uv proved that the decrease of energy gap in the TNTs/PANI composite which as evidenced with Kubelka-Munk calculation equation that was 25 % TNTs/PANI amounting to 3.19 eV and TNTs at 3.24 eV.

**Keywords:** aniline; composite; photocatalyst.

## 1. Introduction

The textile industry is one field that is growing in Indonesia. One of the liquid wastes that usually generated by the textile industry is dye waste which is a non-biodegradable organic compounds, that can cause pollution to the environment, especially the water environment [1]. Various kinds of textile waste pollution conventional

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prevention efforts, such as adsorption and the use of activated sludge have been done, but the results are less effective.

Nanotechnology is one of the rapidly evolving technologies and contributes to the development of material science included in the handling of water pollution by textile waste [2].  $\text{TiO}_2$  is a material that can be applied as photodegradation of organic wastes such as dye textiles [3]. Based on the research conducted by Fujhisima [4], it has been known that the titania is able to accommodate several oxidizing redox potential, so it has a photocatalytic activity and high quantum efficiency and also economical. Other study mentioned that nano  $\text{TiO}_2$  has a limitation in the absorption of visible light because it is only able to absorb UV rays which is only about 5 % of the sunlight [5]. For this reason, there is a need for compounds that can serve as sensitizer to improve the ability of nano  $\text{TiO}_2$  in absorbing the light. Polyaniline is a polymer compound that has a fairly high conductivity and stability. Polyaniline is able to absorb the photon energy and able to transfer electrons. So that, polyaniline can serve as sensitizer to improve performance as the photocatalytic  $\text{TiO}_2$  [5].

## 2. Materials and methods

### 2.1. Materials

TiPP (Titanium IV isopropoxide) 97 % (Sigma-Aldrich), NaOH (Merck), HCl 30 % (Merck),  $\text{CH}_3\text{COOH}$  (Merck), Ethanol 95 %, Ammonium Peroxdisulfat (APS),  $\text{HNO}_3$ , aniline and distilled water, universal indicator (Merck) and the filter paper.

### 2.2. Methods

#### 2.2.1. Synthesis of $\text{TiO}_2$ NPs

Preparation of nano  $\text{TiO}_2$  using sol-gel method with TTiP (Titanium Isopropoxide) precursors. Synthesis was done by dropping the sol B (12 mL distilled water, 18 mL  $\text{C}_2\text{H}_5\text{OH}$ , 18 mL  $\text{CH}_3\text{COOH}$ ) into sol A (30 mL TTiP, 6 mL  $\text{CH}_3\text{COOH}$ , 39 mL  $\text{C}_2\text{H}_5\text{OH}$ ) followed by drop by drop constant stirring for 1 h The process of aging was done as long as 48 h followed by drying the sample by using an oven.  $\text{TiO}_2$  calcination was done at a temperature of 450 °C followed by XRD characterization.

#### 2.2.2. Synthesis TNTs

Titania Nanotubes (TNTs) were prepared from hydrothermal treatment. The preparation was initiated by treating 7.5 g nano- $\text{TiO}_2$  powder with 251 mL of 10 M NaOH followed

by autoclaving at 140 °C in a Teflon-lined autoclave for 24 h. The resultant product was washed many times by distilled water to remove sodium hydroxide, followed by neutralization at pH 7 using 0.1 M HCl and the precipitate dried. Samples followed by calcination at 600 °C. The structure of the obtained material was studied using TEM and XRD.

### 2.2.3. Synthesis of TNTs/PANI

Composites were prepared by chemical oxidative polymerization of aniline with % w/w ratio, where aniline was added as much as 15 %, 20 % and 25 % of the weight of TNTs. As much as 0.5 g TNTs dissolved in 1 M HCl for 30 min. Quantitative aniline (15 %, 20 % and 25 %) was added dropwise into the mixture under vigorously stirring in the ice water bath with the ratio (1:1.5) aniline:APS. Finally the TNTs/PANI (polyaniline) were filtered and washed by using distilled water and ethanol until a neutral pH was reached. Composite TNTs/ PANI dried at a temperature of 80 °C [5]. Samples were characterized using FTIR and DR-UV. In order to confirm the effect of PANI in the composites, samples were tested for the degradation of 5 mg · L<sup>-1</sup> (3 450 to 3 420) cm<sup>-1</sup> rhodamine B. As much as 30 mg TNTs/PANI 15 %, 20 %, 25 % and TNTs dissolved in 30 mL of 5 mg · L<sup>-1</sup> (3 450 to 3 420) cm<sup>-1</sup> rhodamine B that was processed with sonication for 15 min. After sonication, solution was allowed to stand in a dark place for 5 min. Absorbance measurements were done after the compound silenced in dark condition to degradation process using photocatalytic box accompanied stirring for 15 min. The Absorbance measurements were carried out at 5 min, 10 min and 15 min.

### 2.2.4. Characterization material using XRD

Characterization using XRD conducted to determine the degree of crystallinity and particle size. Particle size calculation using equation Debye Scherer (1)

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

### 2.2.5. Characterization TEM

Characterization material doing to analyze the morphology of titania nanotube material. Characterization using TEM SHIMADZU CTLA-4

### 2.2.6. Characterization FTIR

Characterization of polymerization functional groups of aniline is done by using FTIR. analysis performed on the peak polymerization of aniline and TiO<sub>2</sub>

### 2.2.7. Characterization DR-UV

Characterization dr-uv conducted to analyze the changes in the energy gap material TiO<sub>2</sub> and TiO<sub>2</sub>/PANI

## 3. Results and discussion

### 3.1. Characterization of TiO<sub>2</sub> NPs

The crystal structure of the samples was characterized by XRD. Crystallite size of anatase TiO<sub>2</sub> can be calculated from Scherer's formula. Fig. 1 shows diffractogram TiO<sub>2</sub> NPs in a furnace at 450 °C for 3 h. Based on JCPDS card numbers 84-1286 show diffractogram TiO<sub>2</sub>NPs the results of synthesized largely anatas phase. This can be seen from a value of 2θ obtained by the 24.45°; 47.29°; 53.18°; 61.64° for anatase and 54.65°; 74.16° for rutile phase. Through calculations using the equations Debye-Scherer, the size of TiO<sub>2</sub>NPs that we obtained was 13.78 nm.

### 3.2. Characterization of TNTs

The structure of the obtained TNTs was characterized by XRD and TEM.

#### 3.2.1. X-ray diffraction (XRD)

TNTs characterized using XRD to determine particle size and textural coefficient of the material. TNTs diffractogram with a temperature of 600°C was shown in Fig.2. Based on JCPDS Card No. 84-1286, the peak formed indicates that TiO<sub>2</sub> NPs peak at 2θ there are 24.45°; 37.07°; 47.26°; 53.18° is anatase phase and 54.29°; 69.35° is rutile phase. The fields of anatase phase is (101), (004), (105), (200), while rutile phase is (211) and (116). From the analysis of the XRD diffractogram known that any angle of 12° indicating the formation of hydrogen bonds Titanate as research conducted by TNTs [6]. The calculation results showed that the particle size of the TNTs synthesized has a size of 20.53 nm with textural coefficient of 0.9986. From the figure show that TNTs having crystalinity greater than nano TiO<sub>2</sub> NPs.

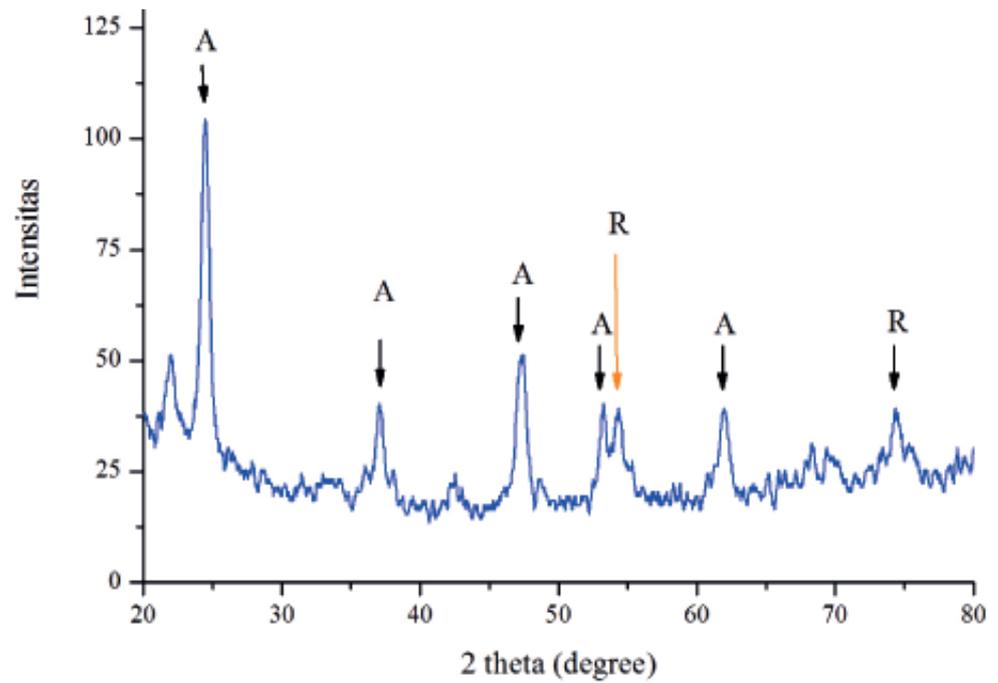


Figure 1: Diffractogram TiO<sub>2</sub> NPs at 450 °C.

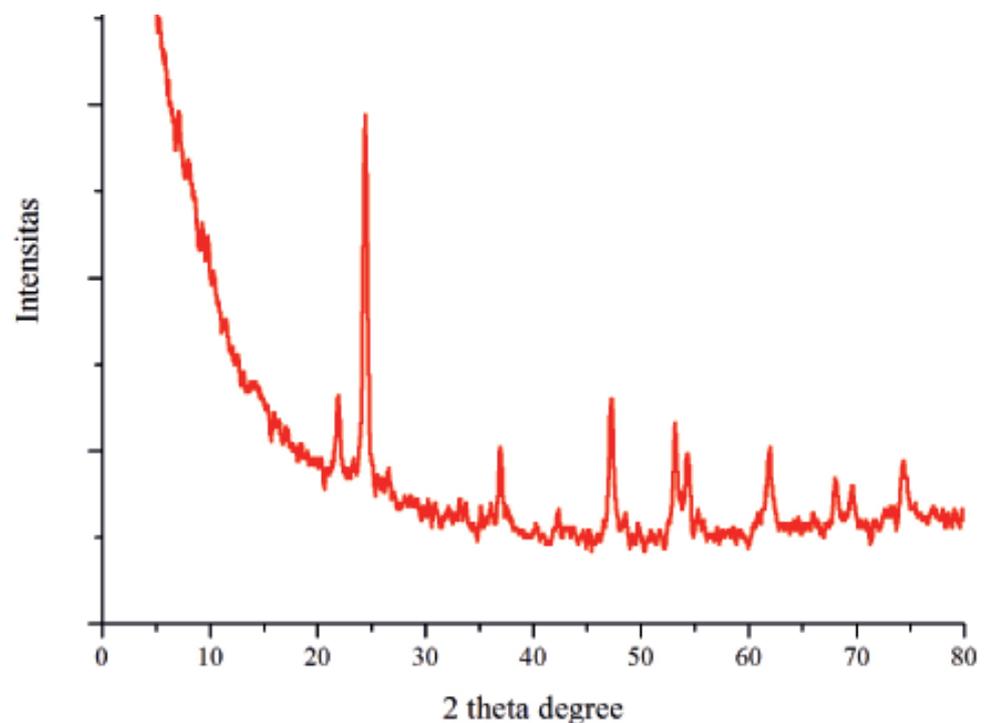
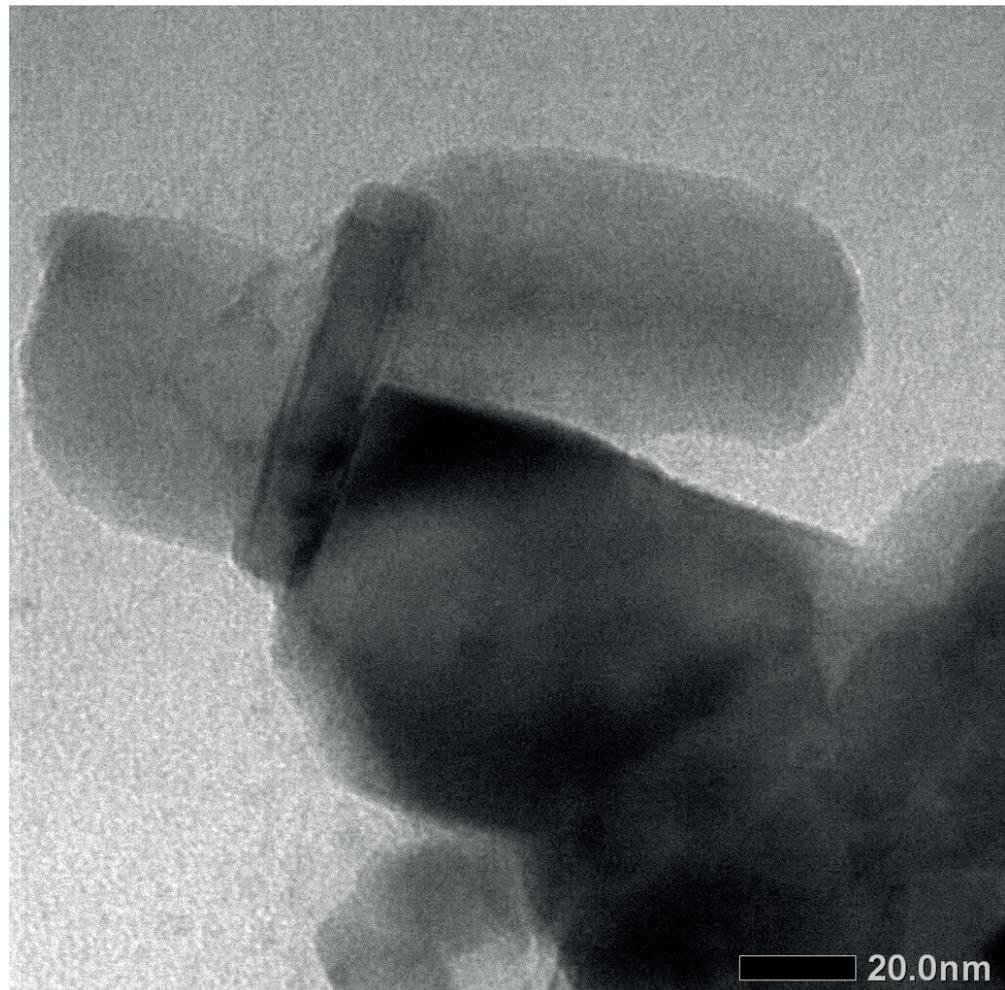


Figure 2: Diffractogram TNTs at 600 °C.

### 3.2.2. Transmission electron microscope (TEM)

Morphology characterization of TNTs using TNTs is as shown in Fig. 3. According to Fig. 3, it can be seen that structure tubes have started to form although the growth



**Figure 3:** Morphology of TNTs at 20 nm magnifications.

of TNTs has not been perfect. It can be seen from the TNTs structure which tend to be short and yet so irregular [7]. The results obtained were quite different to those that had been done by Ashraf et al. [8]. TNTs that are less than the maximum growth is most likely caused by the effect of pressure during the hydrothermal process. The pressure formed during hydrothermal process in addition affected by temperature is also influenced by the percentage of filling the autoclave [9].

### 3.3. Modified TNTs/PANI

Synthesis of TNTs/PANI composites were prepared by chemical oxidative polymerization of aniline [5]. The composites were then characterized using FTIR. Table 1 shows the absorption frequency at  $(3450 \text{ to } 3420) \text{ cm}^{-1}$  which indicates that there is a vibration of N - H bond of the group polyaniline. The absorption frequency at  $(3450 \text{ to } 3420) \text{ cm}^{-1}$  shows the stretching vibration of C = N compounds doped PANI Quinonoid by the number of PANI slightly. The absorption characteristic of  $\text{TiO}_2$  peak appeared

Functional Group	Wavelength Number		
	TNT/PANI 15 %	TNT/PANI 20 %	TNT/PANI 25 %
Vibration N-H	3 433.33	3 427.37	3 425.60
Vibration C=N	1 633.45	1 634.54	1 634.47
Vibration Ti-O-Ti	520.54; 477.13	502.35	478.65

TABLE 1: The functional group composite TNTs/PANI.

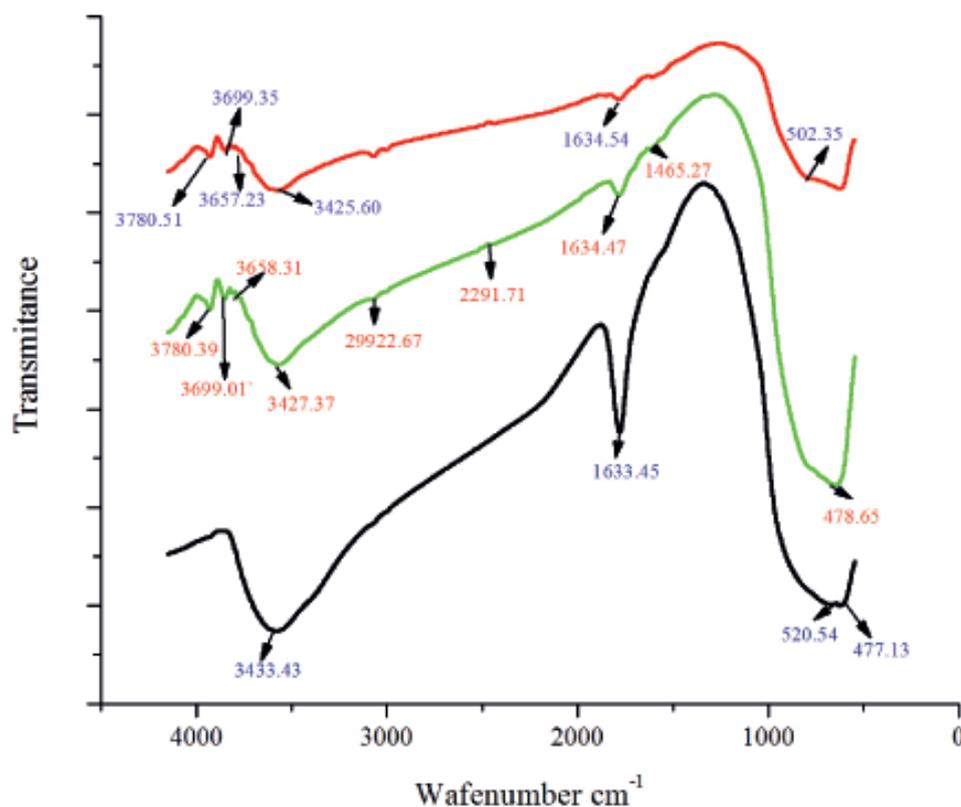


Figure 4: FTIR Spectra of TNTs/PANI (b/b %) 15 %, 20 % and 25 %.

at (500 to 400)  $\text{cm}^{-1}$  where the composites are 15 %, 20 % and 25 % respectively, demonstrated at a wavelength of 520.54  $\text{cm}^{-1}$ ; 502.35  $\text{cm}^{-1}$  and 478.65  $\text{cm}^{-1}$  by [5].

### 3.4. Photocatalytic activity test

The photocatalytic activities of the samples were evaluated by Rhodamine B degradation. Fig. 5 shows the absorbance curve of Rhodamine B at 0 min, 5 min, 10 min and 15 min. In this figure, it is also shown that there is the decline in the concentration of Rhodamine B after photodegradation takes place. In the 0 min before the photodegradation process, largest decrease occurred in the compound TNTs. This is because TNTs have a higher ability to absorb UV light compared to TNTs which have been added with polyaniline in dark condition [5]. But, in the 5 min to 15 min after being

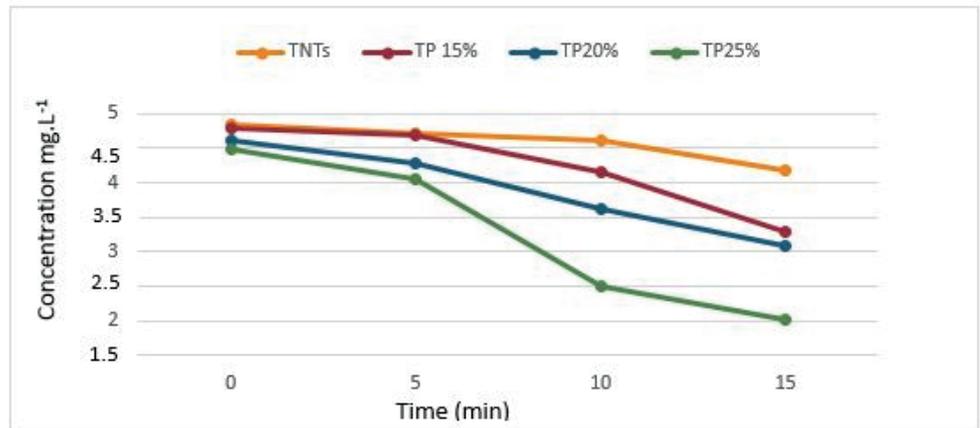


Figure 5: Absorbance Curve of Rhodamin B.

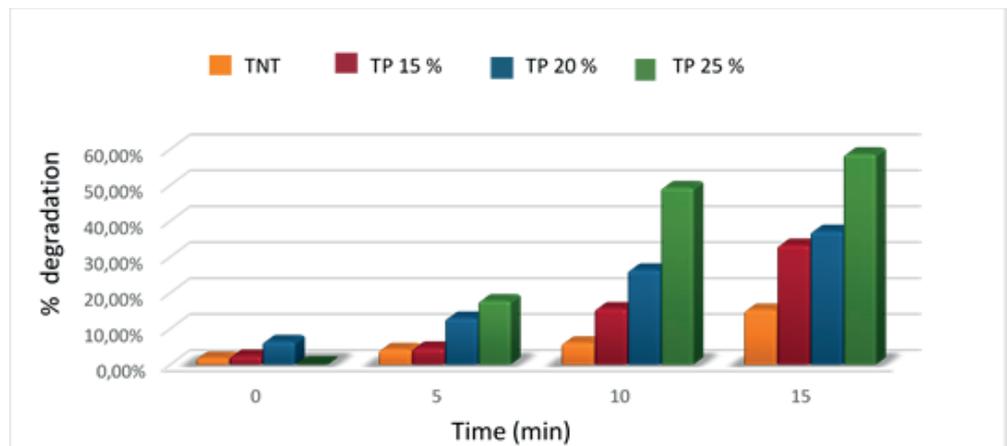


Figure 6: The percentage of Rhodamin B degradation.

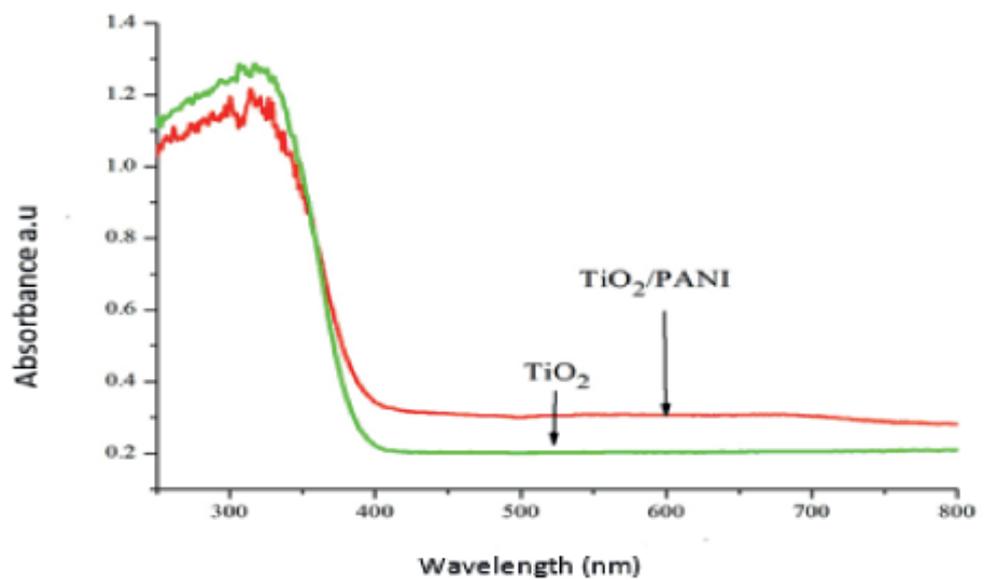


Figure 7: DR-UV spectra.

given the influence of visible light that a decrease in the concentration of rhodamine B with TNTs/PANI higher compared with TNTs. The biggest decline occurred in TNTs polyaniline after the addition of 25 %, 20 % and 15 % respectively. This is in line with the research conducted by Olad et al. [10], which explained that the polyaniline serves as sensitizer, so that it can absorb visible light are more numerous.

Fig. 6 shows that the increase of the degradation percentage of Rhodamine B is proportional to the amount of polyaniline that was added. This is because the addition of polianilin on TNTs causes energy gap on TNTs shrink to ease the process of electron transfer from conduction ribbon to Valence ribbon in the process of degradation of Rhodamine B. TNTs/PANI with the addition of 25 % aniline have the highest rhodamine B degradation activity in amount of 58.73 %. The percentage of rhodamine B degradation after the addition of 20 % and 15 % aniline and without the addition are 37.19 %; 33.33 % and 15.24 % respectively.

### 3.5. Characterization DR-UV

Material 25 % TNTs/PANI, as the best result in the shades of Rhodamine B, were characterized using UV-Vis diffuse reflectance to determine the energy gap and the absorption spectrum. Fig.7 shows that the addition of polyaniline can increase the absorption at the wavelength of visible light. This is according to the research conducted by Xuyen *et al.* [5] which explained that the addition of polyaniline could increase the sensitivity of TNTs as a TNTs photocatalisator with increased ability to absorb visible light. Based on the analysis graph of the absorbance against wavelength (attached), it were obtained values for Eg 3.24 Ev and Eg TNTs material 25 % TNTs/PANI amounted to 3.19 eV. The magnitude of the energy gap (Eg), the energy position of the conduction and valence band will determine the character of a photocatalyst in terms of photon energy requirements required to activate and how the oxidation or the reduction after the power is turned on [11]. Small band gap will allow the particles to jump in the valence band to the conduction band, but also prone to recombination. Electrons are experiencing excitation then migrates towards Polyaniline and trapped in Polinailin so that recombination  $e^- / h^+ + h^+$  can be suppressed and freely diffuse into the surface of a semiconductor.

## 4. Conclusions

- Modification morphology nano TiO<sub>2</sub> to TNT (Titania Nanotube) can improve crystallinity material.

- The addition of polyaniline on TNTs can lower energy gap material. The calculations show energy gap TNTs / PANI 25 % amounted to 3.19 eV and 3.24 eV TNTs.
- Composite TNTs / PANI 25 % have the degradation activity with the largest percent decrease in rhodamine B by 58.73 %.

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