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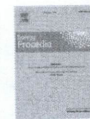
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Synthesis and Characterization of Nitrogen-doped TiO₂ Nanomaterials for Photocatalytic Activities under Visible Light

Siriphan Chainarong^{a, d}, Lek Sikong^{a, d}, Sorapong Pavasupree^c, Sutham Niyomwas^{b, d},  ^a Department of Mining and Materials Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai 90112, Thailand^b Department of Mechanical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai 90112, Thailand^c Department of Materials and Metallurgical Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Pathumthani 12110, Thailand^d NANOTEC Center of Excellence at Prince of Songkla University, Hat Yai 90112, Thailand

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Abstract

Nitrogen-doped TiO₂ nanomaterials were fabricated from hydrogen titanate prepared by hydrothermal method. The starting materials with difference nitrogen sources and concentration were studied. The samples were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), BET surface area, Fourier Transform infrared spectrometer (FT-IR) and UV-vis absorption spectra by UV-VIS spectroscopy. The photocatalytic activity was investigated by degradation of methylene blue aqueous solution under visible light irradiation. The highest photocatalytic activity of nitrogen-doped TiO₂ was gotten from the sample in which 0.5 M guanidine carbonate was used as nitrogen source. Compared with pure TiO₂ (from hydrothermal method) and P25-Degussa, the wavelength range of nitrogen-doped TiO₂ was shifted to visible light while pure TiO₂ and P25-Degussa were showed in ultraviolet region.

Keywords

Nitrogen-doped TiO₂; Photocatalytic Activity; Visible Light; Hydrothermal Method

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Corresponding author. Tel.: +667 428 7196; fax: +667 455 8830.

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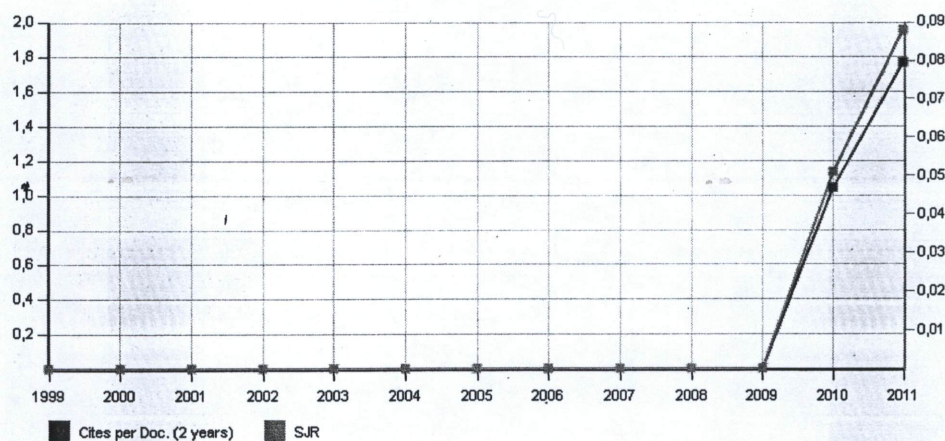
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Synthesis and Characterization of Nitrogen-doped TiO₂ Nanomaterials for Photocatalytic Activities under Visible Light

S. Chainarong, L. Sikong, S. Niyomwas and S. Pavasupree

Abstract— Nitrogen-doped TiO₂ nanomaterials were fabricated from hydrogen titanate prepared by hydrothermal method. The starting materials with difference nitrogen sources and concentration were studied. The samples were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), BET surface area, Fourier Transform infrared spectrometer (FT-IR) and UV-vis absorption spectra by UV-VIS spectroscopy. The photocatalytic activity was investigated by degradation of methylene blue aqueous solution under visible light irradiation. The highest photocatalytic activity of nitrogen-doped TiO₂ was gotten from the sample in which 0.5M guanidine carbonate was used as nitrogen source. Compared with pure TiO₂ (from hydrothermal method) and P25-Degussa, the wavelength range of nitrogen-doped TiO₂ was shifted to visible light while pure TiO₂ and P25-Degussa were shown in ultraviolet region.

Keywords— Nitrogen doped TiO₂, Photocatalytic activity, visible light, Hydrothermal Method

1. INTRODUCTION

Nanostructure titanium dioxide (TiO₂) has attracted great interest because it exhibits many modified electronic and optical properties, and hence resulting extensive applicability in many fields including photocatalysis, environment purification and dye-sensitized solar cell [1], [2]. However, the wide band gap of TiO₂ (anatase of 3.2 eV, rutile 3.0 eV.) limits the absorption wavelength less than 378 nm. Many researchers have done a lot of work to extend the light responsible of TiO₂ from ultraviolet (UV) to the visible light region [3], [7]. From this point, the researcher focused on doping TiO₂ with transition metal and non-metal impurities [8]. Asahi et al. (2001) reported the TiO₂ doping with non-metal ions. They interest the substitutional doping of (C, N, F, P or S) to replace O in the anatase-phase TiO₂ crystal. They prepared TiO_{2-x}N_x powders by treating anatase TiO₂ powder in an NH₃ (67%)/Ar atmosphere at 600 °C for 3h. It was found that to be most effective to reduce band gap [4]-[5]. Y. Nosaka et al. (2005) prepared nitrogen-doped TiO₂ by using organic compounds in deference N source such as urea, Guanidine Hydrochloride and Guanidine Carbonate. The N source of guanidine carbonate was shown the best photocatalytic activity respond under visible light at

wavelength longer than 420 nm. Y. Cong et al. (2006) can be prepared nitrogen-doped TiO₂ by a wet method, i.e., a microemulsion-hydrothermal method. However, the mechanochemical method by using a high-speed ball milling of P25 TiO₂ with nitrogen source such as ammonia solution, hexamine and urea that reported by R. Rattanakam et al. (2009), can absorbed light of wavelength up to 545 nm. Although the particle from mechanochemical method were agglomerated. Nitrogen-doped TiO₂ has been prepared by sputtering, ion implantation, chemical vapor deposition, sol-gel, oxidation of TiN, direct nitridation of TiO₂ [7] and using organic compound. A simple wet chemistry method can be synthesized N-doped TiO₂ nanotubes by treating titanate nanotubes in guanidine carbonate aqueous solution that reported by J. Geng et al. (2009). It was found that the doped nitrogen atoms filled into the lattice of TiO₂ and the absorption edge shifting to visible light region.

In this manuscript, the nitrogen-doped TiO₂ is prepared by hydrothermal method and treating with nitrogen source. The result product from hydrothermal method was hydrogen titanate which will be used as starting material. After that, it was stirred with difference concentration of N source (0.5, 1.0 and 2.0M) from difference N source; i.e., urea and guanidine carbonate. The as-synthesized of nitrogen-doped TiO₂ was followed by heat treatment at 400 °C for 2 h. The obtained powders were characterized and studied their photocatalytic activity under visible light.

2. EXPERIMENTAL PROCEDURE

Preparation of Nitrogen- doped TiO₂

Hydrogen Titanate was prepared by hydrothermal method. In typical procedure, 4 g of commercial TiO₂ powder (Ajax Finechem) and 50 ml of 10M NaOH_(aq) solution were poured into 100 ml of Teflon-line stainless steel autoclave. The autoclave was stirred and maintained

S. Chainarong is with Department of Mining and Materials Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand, E-mail: ch.siriphan@gmail.com

L. Sikong is with Department of Mining and Materials Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand, E-mail: lek.s@psu.ac.th

S. Niyomwas is with Department of Mechanical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand, E-mail: sutham.n@psu.ac.th (corresponding author)

S. Pavasupree is with Department of Materials and Metallurgical Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Thanyaburi, Pathumthani 12110, Thailand, E-mail: sorapongp@yahoo.com

The first three authors are with NANOTEC center of Excellence at Prince of Songkla University, Hat Yai, Songkhla, Thailand 90112

at 130 °C for 24h. Thereafter, the obtained precipitate was washed with distilled water and filtrated for several time. Then, precipitates were transferred into 1L of 0.1M HCl solution and stirred for 24h. This HCl treatment was repeated 3 times and followed by washing with distilled water. After drying at 80 °C in oven, the white hydrogen titanate (denoted as-synthesized TiO_2) was obtained.

Next, 2 grams of as-synthesized TiO_2 were dispersed in 50 ml of aqueous solutions of nitrogen source with different concentration see table 1. After stirring for 24h, the mixture was dried at 80°C in oven and followed by post-heat treatment at 400 °C for 2h. The nitrogen-doped TiO_2 was yellow powders. In case of pure TiO_2 , hydrogen titanate was used as starting material and followed by heat treatment at 400 °C for 2h.

Table 1. Shows Nitrogen-doped Conditions

Nitrogen source	Concentration of Nitrogen source (M)
Guanidine Carbonate (99% Sigma-Aldrich, Germany)	0.5, 1.0, 2.0
Urea (≥ 99 Sigma-Aldrich, Germany)	

Characterization

The phase identification of the as-synthesized and the nitrogen-doped TiO_2 were conducted with X-ray diffraction analysis using X-ray diffractometer (PHILIPS X'Pert MPD). The morphology of samples was observed by transmission electron microscopy (TEM) (JEM-2010, EOL). The Brunauer-Emmett Teller (BET) specific surface area was determined by the nitrogen adsorption (BEL Japan, BELSORP-18Plus). The IR spectra were recorded on a Fourier Transform infrared (FT-IR) spectrometer (Spectrum One, Perkin Elmer). The UV-vis absorption spectra of the samples were recorded using a UV-VIS spectroscopy (UV-2401, Shimadzu).

Photocatalytic activity measurement

The evaluation of the photocatalytic activity of the prepared samples for the photocatalytic decolorization of methylene blue (MB) aqueous solution was performed at room temperature. Experimental process was as follows: the prepared powder samples (0.0375g) were dispersed in a 10 ml MB aqueous solution with a concentration of 1×10^{-5} M in a rectangular cell. Five 10W fluorescence lamps were used as a light source. The concentration of MB aqueous solution was determined by an UV-vis spectrophotometer (Thermo SCIENTIFIC, GENESYS 10UV).

3. RESULT AND DISCUSSION

XRD analysis

Figure 1 shows XRD patterns of as-synthesized TiO_2 and the nitrogen-doped TiO_2 . It was found that the as-synthesized TiO_2 was hydrogen titanate ($\text{H}_2\text{Ti}_3\text{O}_7 \cdot x\text{H}_2\text{O}$) [18]-[20]. After nitrogen-doped and heat treatment process, the samples were decomposed to anatase TiO_2

and $\text{TiO}_2(\text{B})$ (or Monoclinic TiO_2). During solution treatment process, Na^+ ions of $\text{Na}_2\text{Ti}_3\text{O}_7$ was exchanged by H^+ gradually to form $\text{H}_2\text{Ti}_3\text{O}_7$ that was showed in equation (2). The structural changes may be according to following: $\text{H}_2\text{Ti}_3\text{O}_7 \rightarrow 3\text{TiO}_2 + \text{H}_2\text{O}$, due to the protons replaced the sodium ions and facilitated the acid catalyzed condensation of OH groups during heat treatment and lead to formation of TiO_2 [21]. $\text{TiO}_2(\text{B})$ is a metastable polymorph of titanium dioxide, first synthesized by Marchard et al. in 1980 [22], which is formed by the dehydration of layered or tunnel-structured hydrogen titanate ($\text{H}_2\text{Ti}_n\text{O}_{2n+1}$). Later, naturally occurring $\text{TiO}_2(\text{B})$ was also identified in a natural anatase crystal by Banfield. et al.[23]-[25] Thus, this phase is also called "the fourth TiO_2 mineral" or more simply "monoclinic TiO_2 " [26].

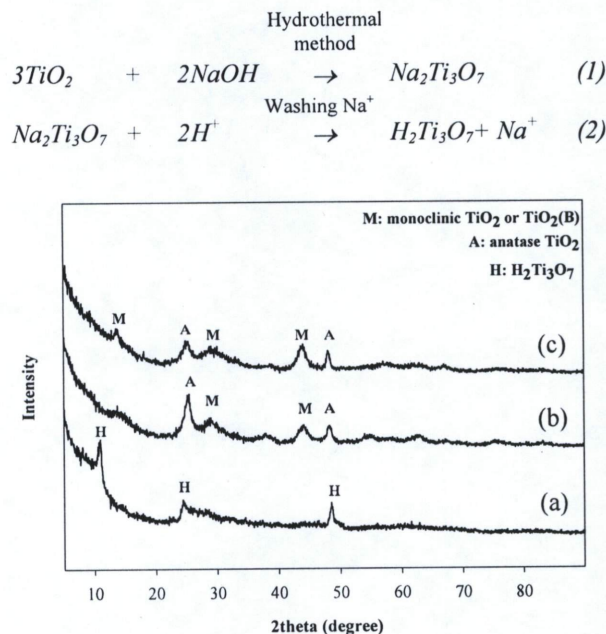


Fig. 1. XRD Patterns of (a) As-synthesized TiO_2 and Nitrogen-doped TiO_2 Samples from Varied Nitrogen Sources: (b) 0.5M Guanidine Carbonate and (c) 0.5M Urea

FT-IR spectrum

FT-IR spectrum of nitrogen-doped TiO_2 samples with different nitrogen sources and concentration are shown in Fig. 2. There are peaks around 3434 to 1630 cm^{-1} that can be assigned to the water and hydroxyl groups [12]-[14]. Low frequency bands were 500 cm^{-1} corresponds to vibration of $\text{Ti}-\text{O}-\text{Ti}$ bond [14]. The peak at 1440 cm^{-1} could be attributed to the nitrogen atoms substitute into TiO_2 network [6], [12]. This peak comes from the N-H bending [16]

UV-Vis absorption spectra

UV-Vis absorption spectra of nitrogen-doped TiO_2 with varied concentration of guanidine carbonate as N source samples, pure TiO_2 from hydrothermal method (denoted as HM- TiO_2) and P25-Degussa were indicated in Fig. 3. The absorbance of all nitrogen-doped TiO_2 shifted to visible light. They showed two absorption edges; the main edge due to the oxide at 390 - 400 nm and weak shoulder due to nitrogen doping at 400 - 500 nm [14]. While the

HM-TiO₂ and P25-Degussa are shown in ultraviolet region (a single sharp edge at 390 and 400 nm, respectively). The absorbance of nitrogen-doped TiO₂ was increased with increased the concentration of guanidine carbonate. The wavelengths were about 395, 400 and 500 nm for 0.5, 1.0 and 2.0M of guanidine carbonate, respectively. The absorption spectra of nitrogen-doped TiO₂ was shifted to visible light due to new electron state above valence band caused by nitrogen doping [4], [8], [15], [17]. Meanwhile, when the nitrogen source was urea with difference concentration that were indicated in Fig. 4, the absorbance also shown in visible light region (two absorption edges). But all samples have shown lower absorbance than guanidine carbonate source. However, the urea source showed absorption spectra higher than HM-TiO₂ and P25-Degussa. As the concentration of urea source increased, the absorption spectra increased.

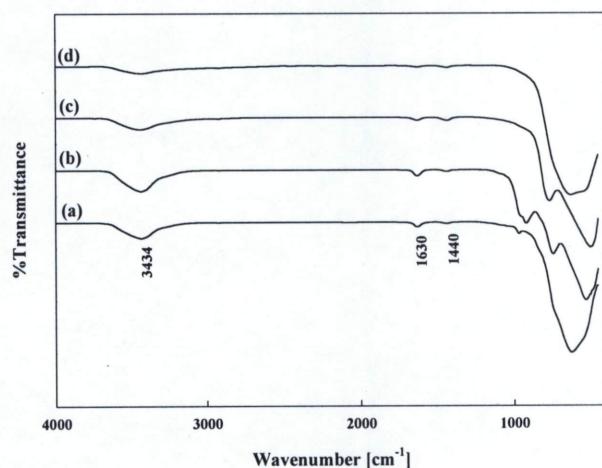


Fig. 2. FT-IR Spectrum of Nitrogen-doped TiO₂ Samples as a Function of Nitrogen Sources with Difference Concentration: (a) 0.5M and (b) 2.0M of Guanidine Carbonate, (c) 0.5M and (d) 2.0M of Urea

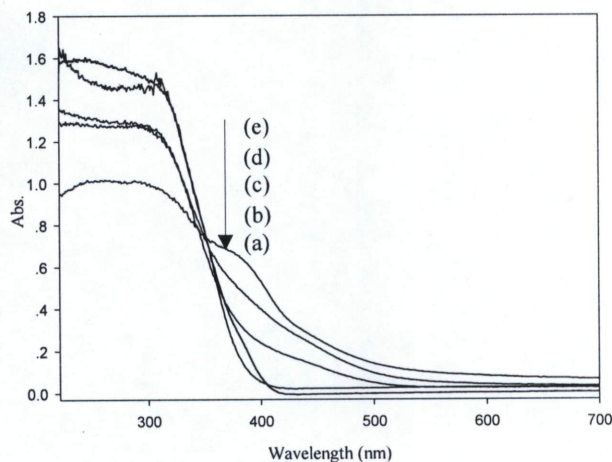


Fig. 3. UV-Vis Absorption Spectra of (a) HM-TiO₂, (b) P25-Degussa and Nitrogen-doped TiO₂ Samples (c) 0.5, (d) 1.0M and (e) 2.0M of Guanidine Carbonate Source

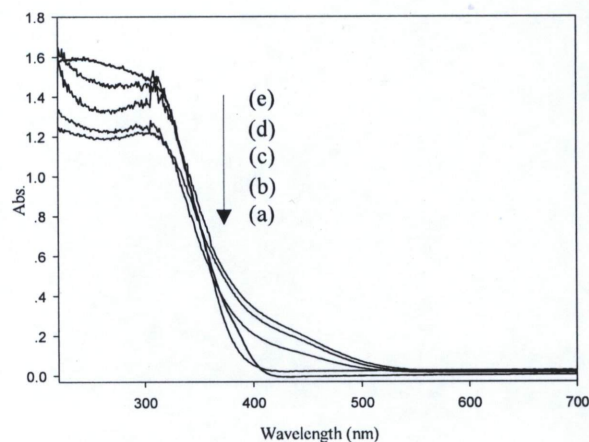


Fig. 4. UV-Vis Absorption Spectra of (a) HM-TiO₂, (b) P25-Degussa and Nitrogen-doped TiO₂ Samples (c) 0.5M, (d) 1.0M and (e) 2.0M of Urea Source

TEM analysis

The morphology of as-synthesized and nitrogen-doped TiO₂ sample are shown in Fig. 5. It was found that the as-synthesized TiO₂ (Fig. 5 (a)) shown in the shape of nanorods about 10-100 nm in diameter and several hundred nanometers in length. For the nitrogen-doped TiO₂ which used 0.5M of guanidine carbonate and followed by heat treatment at 400 °C for 2h shown the cubic nanoparticles of 50-500 nm (Fig. 5(b)). It can be seen that the nanorods were broken to form nanoparticles and growth to form cubic shape when heat treatment at 400 °C [7], [28].

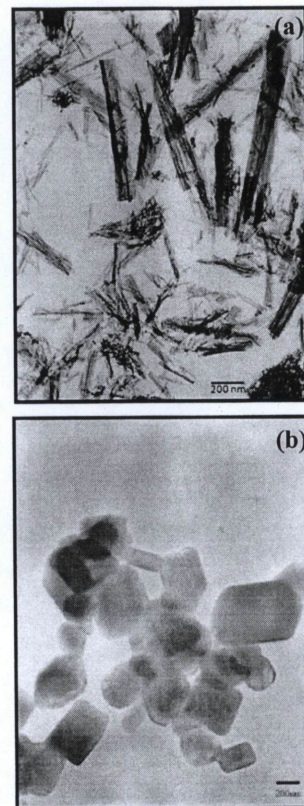


Fig. 5. TEM Images (a) Hydrogen Titanate Powders and (b) Nitrogen-doped TiO₂ (Synthesized from 0.5M of Guanidine Carbonate)

BET surface area

The BET surface area of nitrogen-doped TiO₂ samples (0.5 and 2.0M of guanidine carbonate source) were investigated. When used 0.5M of guanidine carbonate as N source, it was found that surface area was 5.817m²/g. When the concentration of guanidine carbonate was increased to 2.0M, the surface area was decreased to 2.937m²/g. On the other hand, the product from urea source of 0.5M shown surface area around 7.452m²/g. For HM-TiO₂ and P25-Degussa, the surface area was 97.877 and 50m²/g, respectively.

Photocatalytic activity

The photocatalytic activity of nitrogen-doped TiO₂ samples under visible light for MB degradation is compared with HM-TiO₂ and P25-Degussa. Figure 6 shows the relative concentration of MB aqueous solution under photocatalytic activity of nitrogen-doped TiO₂ samples compared with HM-TiO₂ and P25-Degussa. For difference nitrogen source, it was found that guanidine carbonate source (0.5, 1.0 and 2.0M) shows photocatalytic activity higher than urea source (0.5, 1.0 and 2.0M). As the guanidine carbonate source, the photocatalytic activity could degraded of MB aqueous solution to 80-85% in 1h under visible light irradiation. The photocatalytic activity was increased with decreasing the concentration of guanidine carbonate. In addition, the nitrogen-doped TiO₂ powders without irradiation could decolorized MB aqueous solution from 1×10^{-5} M to $\approx 0.25 \times 10^{-5}$ M. Meanwhile, MB aqueous solution was decolorized by urea source higher than HM-TiO₂ and P25-Degussa. For difference concentration of urea source, the photocatalytic activity was increased with decreasing concentration of urea source. Therefore, the photocatalytic activity of nitrogen-doped TiO₂ increased with decreasing the concentration of nitrogen source due to the photocatalytic activity increased with the decrease of doped N atoms in O site, while decreased with decreases of the other site [9].

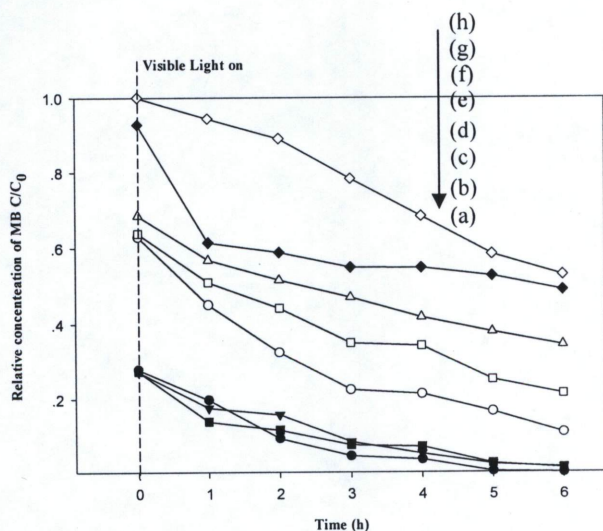


Fig. 6. Photocatalytic Activity of Nitrogen-doped TiO₂ (a) 0.5M, (b) 1.0M, (c) 2.0M of Guanidine Carbonate; (d) 0.5M, (e) 2.0M (f) 1.0M of Urea and Compared with (g) HM-TiO₂ and (h) P25-Degussa.

Wang et al. [27] reported a study based on the relative between particle size and photocatalytic activity of samples. It was found that the higher particle size and lower surface area (21 nm, 70 m²/g) as well as lower particle size and higher surface area (6 nm, 253 m²/g) of the sample were unfavorable for its photocatalytic activity and the samples with intermediate grain size and surface area (11 nm, 157 m²/g) showed the highest photocatalytic activity.

However, the BET surfaces area of the nitrogen-doped TiO₂ powders indicated less than HM-TiO₂ and P25-Degussa while all nitrogen-doped TiO₂ samples was showed the higher photocatalytic activity under visible light. Due to the formation of new electronic state above valence band caused by nitrogen doping, making TiO₂ absorb visible light. The energy of the visible light (> 400 nm) is not sufficient to excite electron from the valence band, as the band gap of TiO₂ corresponds to 385 nm (anatase of TiO₂). After nitrogen-doped, the electron can be excited from new electronic state to the conduction band [4], [15].

4. CONCLUSIONS

Nitrogen-doped TiO₂ powders were successfully synthesized with hydrogen titanate from hydrothermal method that combined with difference concentration and source of nitrogen doping. After that, it was proved the O – N band by FT-IR analysis. The peak at 1430 cm⁻¹ could be attributed to the nitrogen atom embedded in TiO₂ network. The absorbance spectra of nitrogen-doped TiO₂ were shown higher than HM-TiO₂ and P25-Degussa. It can be shifted to visible light region around 400-570 nm when used guanidine carbonate was used as N source at the concentration of 0.5M. The photocatalytic activity under visible light irradiation of nitrogen-doped TiO₂ was increased with increasing concentration of nitrogen source. After nitrogen-doped, the photocatalytic activity was improved greatly compared with P25-Degussa and HM-TiO₂. For optimum condition, 0.5M of guanidine carbonate source was used, it shown percentage degradation of MB aqueous solution at 80% with visible light irradiation for 1h. The morphology of nitrogen-doped TiO₂ is cubic nanoparticles with 50-500 nm in length.

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**SYNTHESIS AND CHARACTERIZATION OF NITROGEN-DOPED
TiO₂ NANOMATERIALS FOR
PHOTOCATALYTIC ACTIVITIES UNDER VISIBLE LIGHT**S. Chainarong¹, L. Sikong¹, S. Niyomwas¹ and S. Pavasupree²¹Prince of Songkla University, Thailand²Rajamangala University of Technology Thanyaburi, Pathumthani, Thailand**Abstract**

Nitrogen-doped TiO₂ nanomaterials were fabricated from hydrogen titanate prepared by hydrothermal method. The starting materials with difference nitrogen sources and concentration were studied. The samples were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), BET surface area, Fourier Transform infrared spectrometer (FT-IR) and UV-vis absorption spectra by UV-VIS spectroscopy. The photocatalytic activity was investigated by degradation of methylene blue aqueous solution under visible light irradiation. The highest photocatalytic activity of nitrogen-doped TiO₂ was gotten from the sample in which 0.5M guanidine carbonate was used as nitrogen source. Compared with pure TiO₂ (from hydrothermal method) and P25-Degussa, the wavelength range of nitrogen-doped TiO₂ was shifted to visible light while pure TiO₂ and P25-Degussa were shown in ultraviolet region.

Keywords—Nitrogen doped TiO₂, Photocatalytic activity, visible light,
Hydrothermal Method