

# Synthesis and Characterization of Nitrogen-doped TiO<sub>2</sub> Nanomaterials for Photocatalytic Activities under Visible Light

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

**Abstract**— Nitrogen-doped TiO<sub>2</sub> 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 TiO<sub>2</sub> was gotten from the sample in which 0.5M guanidine carbonate was used as nitrogen source. Compared with pure TiO<sub>2</sub> (from hydrothermal method) and P25-Degussa, the wavelength range of nitrogen-doped TiO<sub>2</sub> was shifted to visible light while pure TiO<sub>2</sub> and P25-Degussa were shown in ultraviolet region.

**Keywords**— Nitrogen doped TiO<sub>2</sub>, Photocatalytic activity, visible light, Hydrothermal Method

## 1. INTRODUCTION

Nanostructure titanium dioxide (TiO<sub>2</sub>) 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 TiO<sub>2</sub> (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 TiO<sub>2</sub> from ultraviolet (UV) to the visible light region [3], [7]. From this point, the researcher focused on doping TiO<sub>2</sub> with transition metal and non-metal impurities [8]. Asahi et al. (2001) reported the TiO<sub>2</sub> doping with non-metal ions. They interest the substitutional doping of (C, N, F, P or S) to replace O in the anatase-phase TiO<sub>2</sub> crystal. They prepared TiO<sub>2-x</sub>N<sub>x</sub> powders by treating anatase TiO<sub>2</sub> powder in an NH<sub>3</sub> (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 TiO<sub>2</sub> 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 TiO<sub>2</sub> by a wet method, i.e., a microemulsion-hydrothermal method. However, the mechanochemical method by using a high-speed ball milling of P25 TiO<sub>2</sub> 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 TiO<sub>2</sub> has been prepared by sputtering, ion implantation, chemical vapor deposition, sol-gel, oxidation of TiN, direct nitridation of TiO<sub>2</sub> [7] and using organic compound. A simple wet chemistry method can be synthesized N-doped TiO<sub>2</sub> 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 TiO<sub>2</sub> and the absorption edge shifting to visible light region.

In this manuscript, the nitrogen-doped TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub>*

Hydrogen Titanate was prepared by hydrothermal method. In typical procedure, 4 g of commercial TiO<sub>2</sub> powder (Ajax Finechem) and 50 ml of 10M NaOH<sub>(aq)</sub> solution were poured into 100 ml of Teflon-line stainless steel autoclave. The autoclave was stirred and maintained

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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<sub>2</sub>) was obtained.

Next, 2 grams of as-synthesized TiO<sub>2</sub> 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<sub>2</sub> was yellow powders. In case of pure TiO<sub>2</sub>, 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<sub>2</sub> 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

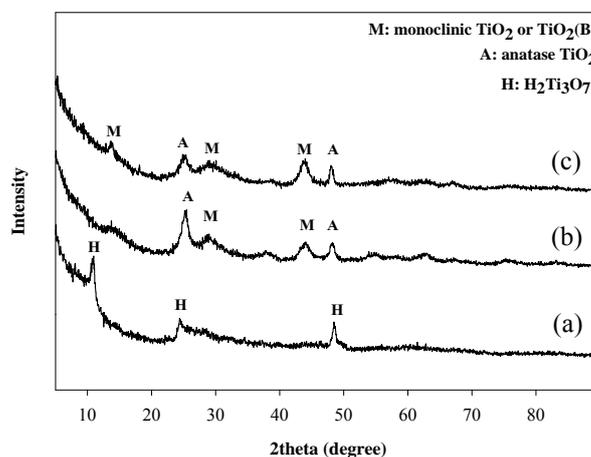
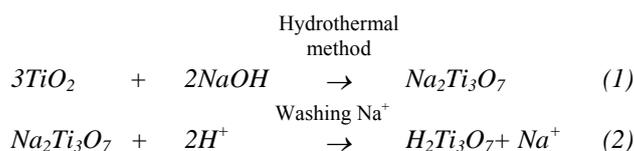
The evaluation of the photocatalytic activity of the prepared samples for the photocatalytic decolorization of methylene blue (MB) aqueous solution was performed at room temperature. Experimental process was as follows: the prepared powder samples (0.0375g) were dispersed in a 10 ml MB aqueous solution with a concentration of 1x10<sup>-5</sup> 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<sub>2</sub> and the nitrogen-doped TiO<sub>2</sub>. It was found that the as-synthesized TiO<sub>2</sub> was hydrogen titanate (H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>·xH<sub>2</sub>O) [18]-[20]. After nitrogen-doped and heat treatment process, the samples were decomposed to anatase TiO<sub>2</sub>

and TiO<sub>2</sub>(B) (or Monoclinic TiO<sub>2</sub>). During solution treatment process, Na<sup>+</sup> ions of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> was exchanged by H<sup>+</sup> gradually to form H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> that was showed in equation (2). The structural changes may be according to following: H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> → 3TiO<sub>2</sub> + H<sub>2</sub>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<sub>2</sub> [21]. TiO<sub>2</sub>(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 (H<sub>2</sub>Ti<sub>n</sub>O<sub>2n+1</sub>). Later, naturally occurring TiO<sub>2</sub>(B) was also identified in a natural anatase crystal by Banfield. et al.[23]-[25] Thus, this phase is also called “the fourth TiO<sub>2</sub> mineral” or more simply “monoclinic TiO<sub>2</sub>” [26].



**Fig. 1. XRD Patterns of (a) As-synthesized TiO<sub>2</sub> and Nitrogen-doped TiO<sub>2</sub> Samples from Varied Nitrogen Sources: (b) 0.5M Guanidine Carbonate and (c) 0.5M Urea**

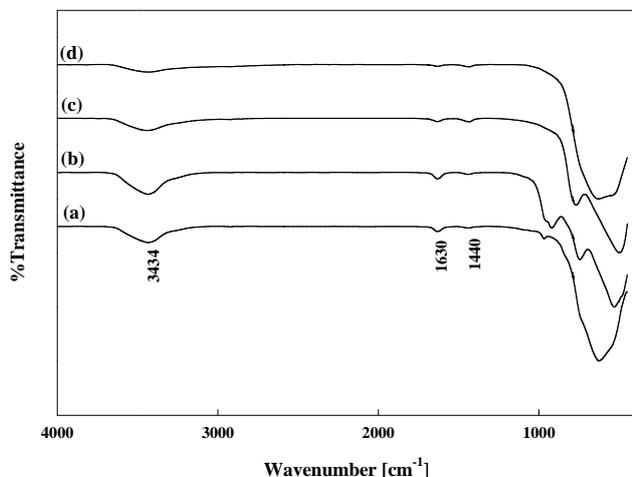
### FT-IR spectrum

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

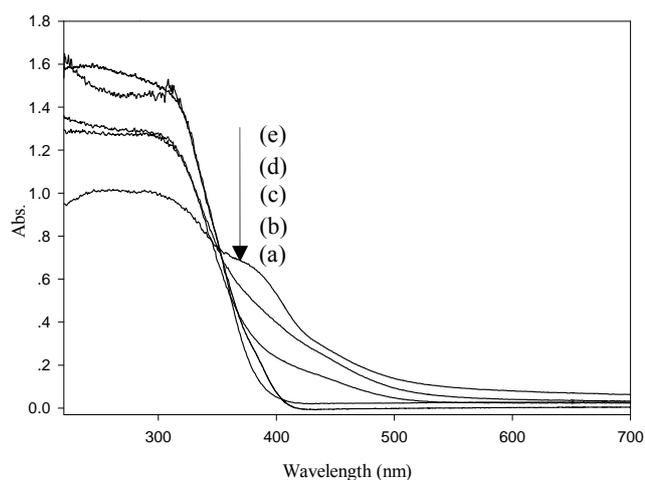
### UV-Vis absorption spectra

UV-Vis absorption spectra of nitrogen-doped TiO<sub>2</sub> with varied concentration of guanidine carbonate as N source samples, pure TiO<sub>2</sub> from hydrothermal method (denoted as HM-TiO<sub>2</sub>) and P25-Degussa were indicated in Fig. 3. The absorbance of all nitrogen-doped TiO<sub>2</sub> 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

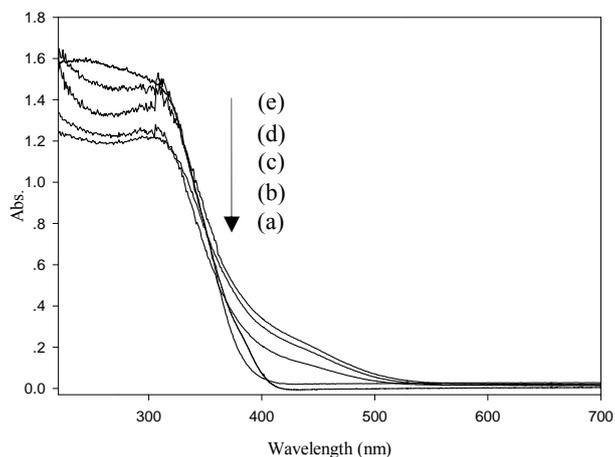
HM-TiO<sub>2</sub> and P25-Deguss are shown in ultraviolet region (a single sharp edge at 390 and 400 nm, respectively). The absorbance of nitrogen-doped TiO<sub>2</sub> was increased with increased the concentration of guanidine carbonate. The wavelengths were about 395, 400 and 500 nm for 0.5, 1.0 and 2.0M of guanidine carbonate, respectively. The absorption spectra of nitrogen-doped TiO<sub>2</sub> 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-TiO<sub>2</sub> and P25-Degussa. As the concentration of urea source increased, the absorption spectra increased.



**Fig. 2.** FT-IR Spectrum of Nitrogen-doped TiO<sub>2</sub> 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



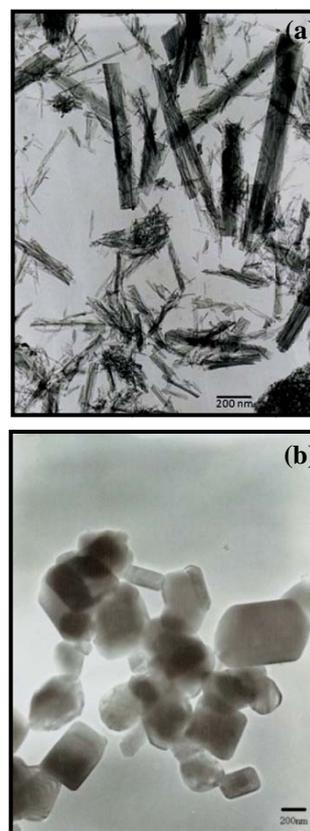
**Fig. 3.** UV-Vis Absorption Spectra of (a) HM-TiO<sub>2</sub>, (b)P25-Degussa and Nitrogen-doped TiO<sub>2</sub> Samples (c)0.5, (d)1.0M and (e) 2.0M of Guanidine Carbonate Source



**Fig. 4.** UV-Vis Absorption Spectra of (a) HM-TiO<sub>2</sub>, (b)P25-Degussa and Nitrogen-doped TiO<sub>2</sub> Samples (c)0.5M, (d)1.0M and (e) 2.0M of Urea Source

**TEM analysis**

The morphology of as-synthesized and nitrogen-doped TiO<sub>2</sub> sample are shown in Fig. 5. It was found that the as-synthesized TiO<sub>2</sub> (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 TiO<sub>2</sub> 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].



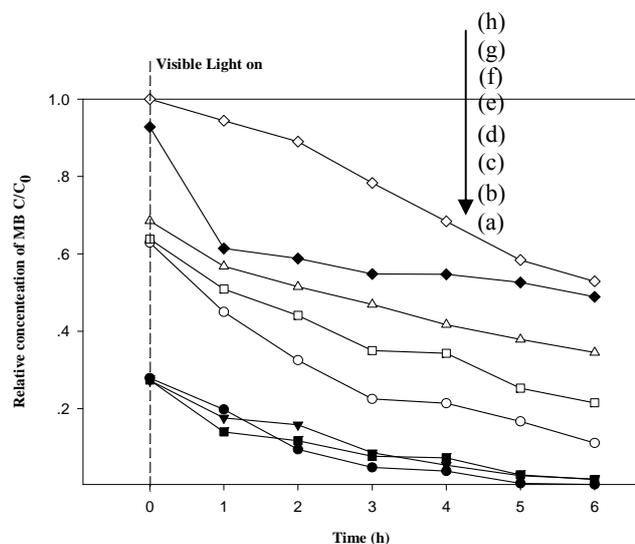
**Fig. 5.** TEM Images (a) Hydrogen Titanate Powders and (b) Nitrogen-doped TiO<sub>2</sub> (Synthesized from 0.5M of Guanidine Carbonate)

### BET surface area

The BET surface area of nitrogen-doped TiO<sub>2</sub> 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 5.817m<sup>2</sup>/g. When the concentration of guanidine carbonate was increased to 2.0M, the surface area was decreased to 2.937m<sup>2</sup>/g. On the other hand, the product from urea source of 0.5M shown surface area around 7.452m<sup>2</sup>/g. For HM-TiO<sub>2</sub> and P25-Degussa, the surface area was 97.877 and 50m<sup>2</sup>/g, respectively.

### Photocatalytic activity

The photocatalytic activity of nitrogen-doped TiO<sub>2</sub> samples under visible light for MB degradation is compared with HM-TiO<sub>2</sub> and P25-Degussa. Figure 6 shows the relative concentration of MB aqueous solution under photocatalytic activity of nitrogen-doped TiO<sub>2</sub> samples compared with HM-TiO<sub>2</sub> 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 TiO<sub>2</sub> powders without irradiation could decolorized MB aqueous solution from 1×10<sup>-5</sup>M to ≈ 0.25×10<sup>-5</sup>M. Meanwhile, MB aqueous solution was decolorized by urea source higher than HM-TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> (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-TiO<sub>2</sub> 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 m<sup>2</sup>/g) as well as lower particle size and higher surface area (6 nm, 253 m<sup>2</sup>/g) of the sample were unfavorable for its photocatalytic activity and the samples with intermediate grain size and surface area (11 nm, 157 m<sup>2</sup>/g) showed the highest photocatalytic activity.

However, the BET surfaces area of the nitrogen-doped TiO<sub>2</sub> powders indicated less than HM-TiO<sub>2</sub> and P25-Degussa while all nitrogen-doped TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> corresponds to 385 nm (anatase of TiO<sub>2</sub>). After nitrogen-doped, the electron can be excited from new electronic state to the conduction band [4], [15].

## 4. CONCLUSIONS

Nitrogen-doped TiO<sub>2</sub> 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<sup>-1</sup> could be attributed to the nitrogen atom embedded in TiO<sub>2</sub> network. The absorbance spectra of nitrogen-doped TiO<sub>2</sub> were shown higher than HM-TiO<sub>2</sub> 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 TiO<sub>2</sub> was increased with increasing concentration of nitrogen source. After nitrogen-doped, the photocatalytic activity was improved greatly compared with P25-Degussa and HM-TiO<sub>2</sub>. 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 TiO<sub>2</sub> is cubic nanoparticles with 50-500 nm in length.

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## REFERENCES

- [1] Wang, D.; Yu, B.; Zhou, F.; Wang, C. and Liu, W. 2009. Synthesis and characterization of anatase TiO<sub>2</sub> nanotubes and their use in dye-sensitized solar cells. *Mater. Chem. Phys.* 113(2-3): 602-606.
- [2] Hsiao, P.; Wang, K., Cheng, C. and Teng, H. 2007. Nanocrystalline anatase TiO<sub>2</sub> derived from a

- titanate-directed route for dye-sensitized solar cells. *J. Photochem. Photobiolo.* 188(1): 19-24.
- [3] Xing, M.; Zhang, J.; and Chen, F. 2009. New approaches to prepare nitrogen-doped TiO<sub>2</sub> photocatalysts and study on their photocatalytic activities in visible light. *Appl. Catal., B* 89(3-4): 563-569.
- [4] Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K. and Tago, A. 2001. Visible-light photocatalysis in nitrogen-doped titanium oxide. *Science*. 293(5528):269-271.
- [5] Jeon, J.; Kim, J. and Ihm, S. 2010. Continuous one-step synthesis of N-doped titania under supercritical and subcritical water conditions for photocatalytic reaction under visible light. *J. Phys. Chem, Solids* 71(4): 608-611.
- [6] Geng, J.; Yang, D.; Zhu, J.; Chen, D. and Jiang, Z. 2009. Nitrogen-doped TiO<sub>2</sub> nanotubes with enhanced photocatalytic activity synthesized by a facile wet chemistry method. *Mater. Res. Bull.* 44(1): 146-150.
- [7] Yan, W.; Jiwei, Z.; Zhenshen, J. and Shunli, Z. 2007. Visible light photocatalytic decoloration of methylene blue on novel N-doped TiO<sub>2</sub>. *Chin. Sci. Bull.* 52(15): 2157-2160.
- [8] Valentin, C.D.; FINAZZI, E., Pacchioni, G.; Selloni, A.; Livraghi, S.; Paganini, M.C. and Giamello, E. (2007). N-doped TiO<sub>2</sub>: Theory and experiment. *Chem. Phys.* 339(1-3): 44-56.
- [9] Nosaka, Y.; Matsushita, M.; Nishino, J. and Nosaka, A.Y. 2005. Nitrogen-doped titanium dioxide photocatalysts for visible response prepared by using organic compounds. *Sci. Technol. Adv. Mater.* 6(2): 143-148.
- [10] Cong, Y.; Xiao, L.; Zhang, J.; Chen, F. and Anpo, M. 2006. Preparation and characterization of nitrogen-doped TiO<sub>2</sub> photocatalyst in different acid environments. *Res. Chem. Intermed.* 32(8): 717-724.
- [11] Rattanakam, R. and Supothina, S. 2009. Visible-light-sensitive N-doped TiO<sub>2</sub> photocatalysts prepared by a mechanochemical method: effect of a nitrogen source. *Res. Chem. Intermed* 35(3); 263-269.
- [12] Xu, J.; Dai, W.; Li, J.; Cao, Y.; Li, H.; He, H. and Fan, K. 2008. Simple fabrication of thermally stable aperture N-doped TiO<sub>2</sub> microtubes as a highly efficient photocatalyst under visible light irradiation. *Catal. Commun.* 9(1): 146-152.
- [13] Hu, S.; Wang, A.; Li, X. and Löwe, H. 2010. Hydrothermal synthesis of well-dispersed ultrafine N-doped TiO<sub>2</sub> nanoparticles with enhanced photocatalytic activity under visible light. *J. Phys. Chem. Solids*. 71(3): 156-162.
- [14] Shao, G.; Zhang, X. and Yuan, Z. 2008. Preparation and photocatalytic of hierarchically mesoporous-macroporous TiO<sub>2-x</sub>N<sub>x</sub>. *Appl. Catal., B* 82(3-4): 208-218.
- [15] Wu, Z.; Dong, F., Zhao, W. and Guo, S. 2008. Visible light induced electron transfer process over nitrogen doped TiO<sub>2</sub> nanocrystals prepared by oxidation of titanium nitride *J. Hazard. Mater.* 157(1): 57-63.
- [16] Matsumoto, T.; Iyi, N.; Kaneko, Y.; Kitamura, K.; Ishihara, S.; Takasu, Y. and Murakami, Y. 2007. High visible-light photocatalytic activity of nitrogen-doped titania prepared from layered titania/isosterate nanocomposite. *Catal. Today*. 120(xx): 226-232.
- [17] Livraghi, S.; Paganini, M.C.; Giamello, E.; Selloni, A.; Valentin, C.D.; Pacchioni, G. 2006. Origin of photo-activity of nitrogen-doped titanium-dioxide under visible light. *J. Am. Chem. Soc.* 128(49): 15666-15671.
- [18] Yoshida, R.; Suzuki, Y. and Yoshikawa, S. 2005. Syntheses of TiO<sub>2</sub>(B) nanowires and TiO<sub>2</sub> anatase nanowires by hydrothermal and post-heat treatments. *J. Solid State Chem.* 175(7): 2179-2185.
- [19] Wang, D.; Zhou, F.; Wang, C. and Liu, W. 2008. Synthesis and characterization of silver nanoparticle loaded mesoporous TiO<sub>2</sub> nanobelts. *Microporous Mesoporous Mater.* 116(1-3): 658-664.
- [20] Suzuki, Y.; Pavasupree, S.; Yoshikawa, S. and Kawahata, R. 2005. Natural rutile-derived titanate nanofibers prepared by direct hydrothermal processing. *J. Mater. Res.* 20(4): 1063-1070.
- [21] Qamar, M.; Yoon, C.R.; Oh, H.J.; Lee, N.H.; Park, K.; Kim, D.H.; Lee, K.S.; Lee, W.J. and Kim, S.J. 2008. Preparation and photocatalytic activity of nanotubes obtained from titanium dioxide. *Catal. Today* 131(1-4): 3-14.
- [22] Marchand, R.; Brohan, L. and Tournoux, M. 1980. TiO<sub>2</sub> (B) A New Form of Titanium Dioxide and the Potassium Octatitanate K<sub>2</sub>Ti<sub>8</sub>O<sub>17</sub>. *Mater. Res. Bull.* 15(8): 1129-1133.
- [23] Banfield, J.F.; Veblen, D.R. and Smith, D.J. 1991. The Identification of Naturally Occuring TiO<sub>2</sub> (B) by Structure Determination Using High-Resolution Electron Microscopy, Image Simulation, and Distance-Least-Squares Refinement. *Am. Mineral.* 76(44): 343-353.
- [24] Banfield, J.F. and Veblen, D.R. 1992. Conversion of Perovskite to Anatase and TiO<sub>2</sub> (B): A TEM Study and the Use of Fundamental Building-Blocks for Understanding Relationship among the TiO<sub>2</sub> Minerals *Am. Mineral.* 77: 545-557.
- [25] Banfield, J.F.; Bischoff, B.L. and Anderson, M.A. 1993. TiO<sub>2</sub> Accessory Minerals: Coarsening, and Transformation Kinetics in Pure and Doped Synthetic Nanocrystalline Materials. *Chem, Geology.* 110(1-3): 211-231.
- [26] Yin, S.; Fujishiro, Y.; Wu, J.; Aki, M. and Sato, T. 2003. Synthesis and Photocatalytic Properties of Fibrous Titania by Solvothermal Reactions. *J. Mater. Proc. Tech.* 137(1-3): 45-48.
- [27] Wang, C.C.; Zhang, Z. and Ying, J.Y. 1997. Photocatalytic Decomposition of Halogenated Organics Over Nanocrystalline Titania. *Nanostruct. Mater.* 9(1-8): 583-586.
- [28] Yu, A.; Wu, G. and Zhang, F. 2009. Synthesis and Characterization of N-doped TiO<sub>2</sub> Nanowires with Visible Light Response. *Catal. Lett.* 129(3-4): 507-512.