TẠP CHÍ KHOA HỌC
TRƯỜNG ĐẠI HỌC QUY NHƠN

Khảo sát ảnh hưởng nhiệt độ nung đến khả năng quang xúc tác phân hủy dung dịch tetracycline của vật liệu TiO_2 đồng pha tạp (C, N, S)

Nguyễn Thị Lan[1,*], Võ Hoàng Anh[1], Nguyễn Văn Thắng[1], Lê Thị Cẩm Nhung[1], Lê Thị Thanh Thúy,[1] Nguyễn Phi Hùng[2]

[1]*Khoa Khoa học Tự nhiên, Trường Đại học Quy Nhơn, Việt Nam*
[2] *Viện Khoa học giáo dục, Trường Đại học Quy Nhơn, Việt Nam*

Ngày nhận bài: 05/03/2020; Ngày nhận đăng: 05/04/2020

TÓM TẮT

Vật liệu nano TiO_2 pha tạp C, N, S (TH-TiO_{2-a}) được tổng hợp bằng phương pháp thủy nhiệt sử dụng tiền chất là $TiOSO_4$ và thiourea điều chế từ quặng Ilmenite. Ảnh hưởng của nhiệt độ nung đến khả năng phân hủy quang xúc tác tetracyline của vật liệu TH-TiO_{2-a} được khảo sát một cách hệ thống. Hoạt tính quang xúc tác được đánh giá qua sự phân hủy kháng sinh tetracycline nồng độ 30 mg/L dưới ánh sáng khả kiến. Kết quả thực nghiệm cho thấy nhiệt độ nung đóng một vai trò quan trọng trong quá trình kết tinh của vật liệu. Mẫu TiO_2 pha tạp C, N, S nung ở 500^{o}C trong không khí, thời gian 1 giờ cho hiệu quả quang xúc tác tốt nhất. Đáng chú ý là việc nung mẫu ở 500^{o}C đã làm tăng độ tinh thể hóa, loại bỏ hiệu quả dư lượng chất hữu cơ trên bề mặt, điều khiển kích thước hạt thích hợp, và cải thiện đáng kể hoạt tính quang xúc tác.

Từ khóa: *TiO_2, Anatase, quang xúc tác, tetracycline.*

**Tác giả liên hệ chính.*
Email: nguyenthilan@qnu.edu.vn

JOURNAL OF SCIENCE
QUY NHON UNIVERSITY

Influence of the annealing temperature on the tetracycline photocatalytic degradation of (C, N, S) co-doped TiO_2 materials

Nguyen Thi Lan[1,*], Vo Hoang Anh[1], Nguyen Van Thang[1], Le Thi Cam Nhung[1], Le Thi Thanh Thuy[1], Nguyen Phi Hung[2]

[1]Faculty of Natural Sciences, Quy Nhon University, Vietnam
[2]Institute of Education Science, Quy Nhon University, Vietnam

Received: 05/03/2020; Accepted: 05/04/2020

ABSTRACT

C, N and S co-doped TiO_2 samples (TH-TiO_{2-a}) were synthesized by the hydrothermal method using thiourea and $TiOSO_4$ prepared from Ilmenite ore. The influence of the annealing temperature on the tetracycline photocatalytic degradation of the TH-TiO_{2-a} samples was systematically investigated. Photocatalytic activities of all samples were evaluated by the photodegradation of tetracycline antibiotics at 30 mg/L under the visible light irradiation. It is found that the annealing temperature plays an important role in the crystallization of the samples. The C, N and S co-doped TiO_2 sample annealed at 500°C in air for 1 hour exhibits the best photocatalytic activity. It is worth mentioning that annealing at 500°C improves crystallinity, effectively eliminates organic residues on the surface, controls particle sizes, and significantly improves the photocatalytic activity of the obtained sample.

Keywords: *TiO_2, Anatase, Photocatalyst, Tetracycline*.

1. INTRODUCTION

Titanium and titanium dioxide are applied in many fields such as aerospace, space, ship, chemicals (production of paper, paint, plastic, rubber, ink, soap, cosmetic, pharmaceutical,...), food processing, medical instruments, photo-catalytic treatment of organic pollutants,...[1] Currently, there are many methods for fabricating nano-sized TiO_2 such as chemical vapor deposition (CVD), oxidation of titanium tetrachloride (known as the chloride process), sol-gel method and thermal treatment or hydrolysis of titanium alkoxides.[2-5] However, these methods require not only expensive titanium sources but also stringent synthesis conditions, and thereby hindering them from practical applications. Ilmenite ore is known as a cheap, non-toxic and widely distributed material source in the world, in which Vietnam is one of the countries with large reserves of titanium. Therefore, it is highly desirable to fabricate nano-sized TiO_2 from Ilmenite ore. Nowadays, titanium dioxide (TiO_2) is mainly used for the photocatalytic decomposition of organic pollutants. However, the band gap of TiO_2 is wide (3.0 eV for the rutile phase and 3.2 eV for the anatase phase), which is not suitable for the visible light irradiation, so TiO_2 only shows photocatalytic activities in the ultraviolet light region.

Besides, the rate of electron-hole recombination in TiO_2 is relatively fast, limiting its photocatalytic efficiency. To overcome these

**Corresponding author.*
Email: nguyenthilan@qnu.edu.vn

disadvantages, many studies have been done such as denaturing TiO_2 by Fe, Mn, Zn...[6, 7] or combining with other materials to prepare composites such as TiO_2/MoO_3,[8] TiO_2/MoS_2,[9] … In particular, many recent reports have demonstrated that the introduction of non-metals such as N, C, S, P and halogen into the TiO_2 structure leads to an increase in the photocatalytic activities of TiO_2 in the visible light region. In fact, the modification of TiO_2 with carbon increases the photosensitivity of the obtained material[10] while the modification with nitrogen and sulfur reduces the band gap energy of TiO_2, thereby improving the photocatalytic activities under the illumination of the visible light.[11] However, these studies only use commercial TiO_2 sources, very few studies on TiO_2 denaturation from Ilmenite ore.[12] In this present work, C, N and S co-doped TiO_2 samples were synthesized from $TiOSO_4$ (prepared from Ilmenite ore of Binh Dinh) by the hydrothermal method. The hydrothermal method was chosen for this work due to the fact that this method has a number of advantages over other methods, such as low energy consumption, low cost, high speed of reaction, and simple and environmentally friendly process. It should be noted that, this method allows controlling the structure of the obtained materials by tailoring hydrothermal parameters. Therefore, in this work, the influence of the annealing temperature on the photodegradation of tetracycline was systematically investigated.

2. EXPERIMENT

2.1. Materials synthesis

Starting materials: Binh Dinh Ilmenite ore, concentrated sulfuric acid H_2SO_4 (Guangdong, China), distilled water, thiourea CH_4N_2S (Guangdong China), tetracycline $C_{22}H_{24}O_8N_2.HCl$ (Institute of Drug Quality Control Ho Chi Minh City, Vietnam).

2.1.1. Synthesis of TH-TiO_2

2.27 grams of $TiOSO_4$ prepared from Binh Dinh Ilmenite ore [13] was put into Teflon flask before adding a defined amount of thiourea (with molar ratio of thiourea to TiO_2 = 2:1) and 180 mL of distilled water. The Teflon flask was put in the autoclave and dried at 180°C for 12 hours.[14] After the hydrothermal process, the autoclave was naturally cooled to room temperature. The obtained white precipitate was filtered and washed several times with distilled water until the water has a constant pH before annealing at different temperatures (400, 500, 600, and 700 °C) for 1 hour. The obtained materials were denoted as TH-$TiO_{2\text{-}a}$ (a = 400, 500, 600 and 700°C).

2.1.2. Synthesis of TiO_2

The TiO_2 sample was also prepared under the same conditions as the TH-$TiO_{2\text{-}a}$ without the addition of thiourea.

2.2. Photocatalytic evaluation

The photocatalytic activities of the obtained samples were evaluated through the photocatalytic decomposition of tetracycline (30 mg/L) with the catalytic concentration of 0.6 g/L. The mixture was magnetically stirred in the dark for 30 minutes to reach an absorption-desorption equilibrium, before illuminating with a 60 W filament lamp (filter cutoff $\lambda > 420$). The remaining tetracycline concentrations as a function of the iradiation time was determined by HPLC-UV method at a wavelength of about 355 nm.

Tetracycline photodegradation efficiency of the obtanined samples is calculated by the following formula:

$$H = \frac{C_o - C}{C_o}.100 \qquad (1)$$

In which, C_o is the initial concentration of tetracycline and C is the remaining concentration of tetracycline after each corresponding time.

2.3. Materials characterization

The phase identification of the obtained materials as done by X-ray diffraction method using a D8 Advance Brucker diffractometer operated at 40 kV and 100 mA with Cu-Kα radiation ($\lambda_{K\alpha}$ = 1,5406Å),

and the crystallite size is calculated from the Debye - Scherrer equation $\bar{r} = \frac{0,89 . \lambda}{\beta . \cos\theta}$ (2). The infrared (IR) spectra were recorded on GX-PerkinElmer. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) images were taken on Nova Nano SEM 450 and JEOL JEM 1010, respectively to investigate the surface morphology of the obtained samples. Specific surface area of all samples was measured on Micromeritics ASAP 2000 Equipment at the Institute of Chemistry, Vietnam Academy of Science and Technology. Tetracycline concentration was determined by HPLC-UV method at λ = 355 on Thermo Scientific series 3300 HPLC (Thermo Scientific Technologies, CA, USA).

3. RESULTS AND DISCUSSION

3.1. Materials characterization

IR spectra in the absorption range from 400 - 4000 cm^{-1} for TH-TiO_{2-500} và TiO_{2-500} samples are shown in Figure 1. IR spectra of both samples has a absorption band around 400 - 700 (860) cm^{-1} due to the valence oscillation of Ti-O-Ti bond.[15, 16] The peaks at 3550 and 1518 cm^{-1} are due to the valence and deformation fluctuations of the hydroxy group of water adsorbed on the surface of the samples. [17, 18] The peak around 1400 cm^{-1} of the doped sample is attributed to the oscillation of NH_4^+ ions.[19] Compared with the TiO_{2-500} sample, the TH-TiO_{2-500} sample has additional absorption peaks at 2982, 2320, 1992, 1712, 1634, and 1050 cm^{-1}, suggesting the formation of new bonds on the TiO_2 crystal lattice structure after doping. The peak at 1050 cm^{-1} corresponds to the oscillation of the Ti-O-S bond [20-22] and thereby indicating that S atoms has entered in the TiO_2 crystal structure. In addition, the peak at 1992 cm^{-1} of the TH-TiO_2 sample may be due to the formation of new compounds during the thiourea decomposition. The characteristic peak observed at 2320 cm^{-1} is related to the oscillation of the C = O group of CO_2 present in the air. The band around 1712 cm^{-1} corresponds to the carbonyl group, the peak at 2982 cm^{-1} corresponds to the C-H bond [18, 23, 24] and the peak near 1634 cm^{-1} is due to the bending vibration of the N-H bond.[25, 26] These peaks were not observed in the TiO_{2-500} sample, suggesting that C, N, S has been successfully doped into the crystal structure of TiO_2.

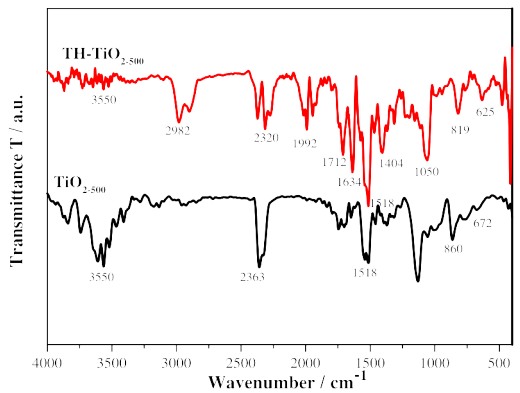

Figure 1. IR spectra for TH-TiO_{2-500} and TiO_{2-500}

The influence of the annealing temperature on the crystal structure of TH-TiO_{2-a} samples annealed at between 400-700°C was investigated by XRD and the obtained XRD patterns are shown in Figure 2.

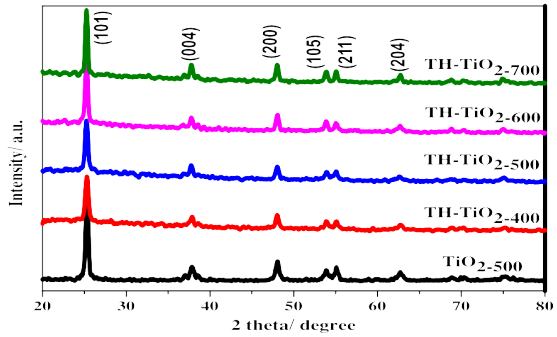

Figure 2. XRD patterns for TH-TiO_{2-a} annealed at different temperatures

It is found that all TH-TiO_{2-a} samples crystallized in the anatase phase, no rutile or brookite phases are observed. As the annealing temperature increases from 400 to 700°C, the (101) peak intensity increases and the spectral line half width at the (101) plane became narrower, resulting in a larger crystallite size. This proves that TiO_2 anatase gradually crystallizes as the annealing temperature increases.[27] The average crystallite size of the TH-TiO_{2-a} samples was

calculated by Scherrer's equation and presented in Table 1. It should be noted that the average crystallite size of all doped samples is smaller than of the un – doped sample $TiO_{2\text{-}500}$. This suggests that co-doping C, N and S into TiO_2 prevents the grain growth which is in good agreement with previous reports. [20, 21, 28, 29]

The specific surface area and porosity of the obtained samples were determined by the BET method and their results are presented in Figure 3.

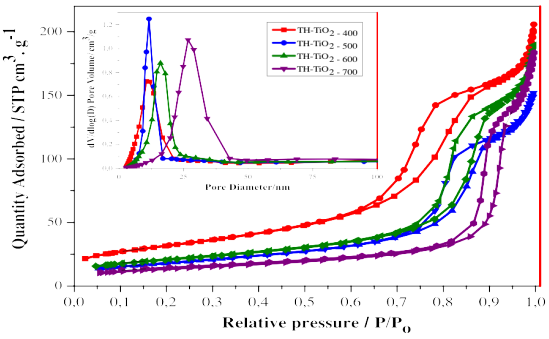

Figure 3. N_2 adsorption-desorption isotherms at 77 K and pore diameter distribution curves of the TH-$TiO_{2\text{-}a}$ samples according to BJH

The N_2 adsorption-desorption isotherms at 77K of the TH-$TiO_{2\text{-}a}$ samples shown in Figure 3 belong to IV type with type H1 loops (according to IUPAC classification). This is characteristics for material systems with the mesoporous structure formed by the particles intersecting with cylindrical-like canal systems or created by agglomeration of spherical particles.

The specific surface area determined according to the BET method for the TH-$TiO_{2\text{-}a}$ samples annealed at 400 - 700 ^oC is 73.47, 92.25, 65.20 and 47.35 m^2/g, respectively.

The N_2 adsorption-desorption isotherms of the TH-$TiO_{2\text{-}a}$ samples begin to condense at the relative pressure P/P_0 of about 0.7-0.95, in which TH-$TiO_{2\text{-}500}$ sample has capillary condensation phenomenon at a relatively lower pressure than the others, indicating that this sample has narrower capillaries. This is consistent with data on the average pore diameter calculated by the BJH method of the TH-$TiO_{2\text{-}a}$ samples (13.81, 10.46, 15.13 and 24.30 nm for the sample annealed at 400, 500, 600 and 700^{o}C, respectively).

In addition, it is found that except for the TH-$TiO_{2\text{-}500}$ sample the specific surface area of the TH-TiO_2 samples decreases as a function of the annealing temperature. This may be because a change in the annealing temperature results in a change in the particle size and consequently a change in the specific surface area. Indeed, Carp et al reported that the activation energy decreases for increasing the annealing temperature, so the growth speed of the grain is large and the particle size increases rapidly at the high temperature. In contrast, at the low annealing temperature, the activation energy is large, so the particle growth rate is slower. As a result, the particle size of the obtained materials is small.[30]

The surface morphology of the TH-$TiO_{2\text{-}a}$ samples are characterized by TEM and SEM methods and the results are shown in Figure 4 and Figure 5 (a-e). As can bee seen in Figure 4, the obtained samples have a structured morphology, the particles are spherical, quite uniform. SEM images also indicate that as the annealing temperature increases, the particle size of the TH-$TiO_{2\text{-}a}$ samples increases.

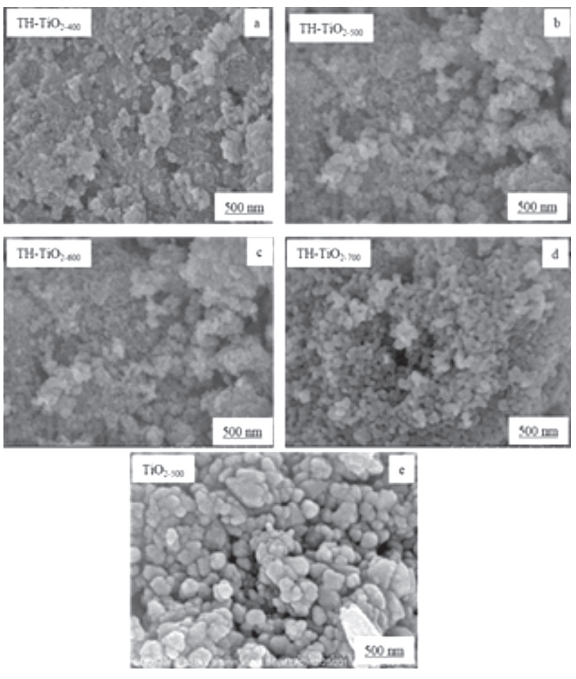

Figure 4. SEM images of TH-$TiO_{2\text{-}400}$ (a), TH-$TiO_{2\text{-}500}$ (b), TH-$TiO_{2\text{-}600}$ (c), TH-$TiO_{2\text{-}700}$ (d), and $TiO_{2\text{-}500}$ (e)

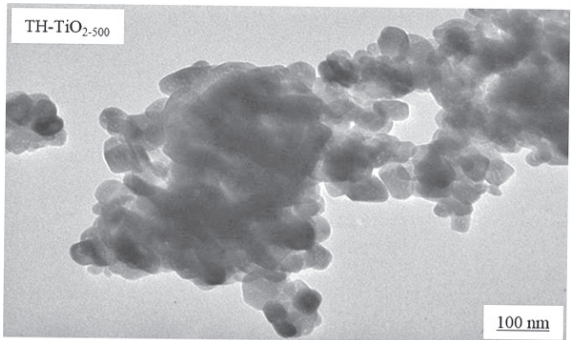

Figure 5. TEM image of TH-TiO_{2-500}

UV-Vis DRS was employed to investigate the influence of the annealing temperature on the light adsorption of the TH-TiO_{2-a} samples and their UV-Vis DRS spectra are shown in Figure 6. As can be seen in Figure 6 there is a redshift as a function of the annealing temperature. This may be due to the evaporation of the doped elements as the annealing temperature increases.[31] Particularly, TH-TiO_{2-400} và TH-TiO_{2-500} samples have strong absorption in the visible light region. This is because the three doping of C, N and S has narrowed the band gap energy of TiO_2 and created many carriers [21, 32]. The band gap energy of all samples was calculated based on the Kubelka-Munk equation and shown in Table 1 and Figure 7. Accordingly, the band gap of the TH-TiO_{2-a} samples annealed at 400 – 700°C is 2.86, 2.88, 3.02, and 3.05, respectively, which is lower than that of the TiO_{2-500} sample (3.2 eV). The decrease in the band gap energy after doping may be attributed to the occurrence of the hybridized states of doped elements (C, N and S) in the band gap of the doped samples.[32, 33]

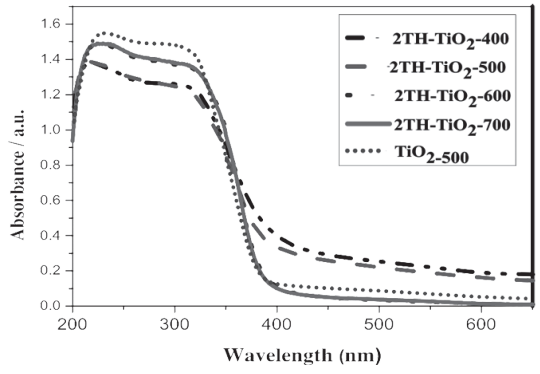

Figure 6. UV-Vis- DRS spectra for TH-TiO_{2-a} (a = 400, 500, 600, 700 °C) and TiO_{2-500}.

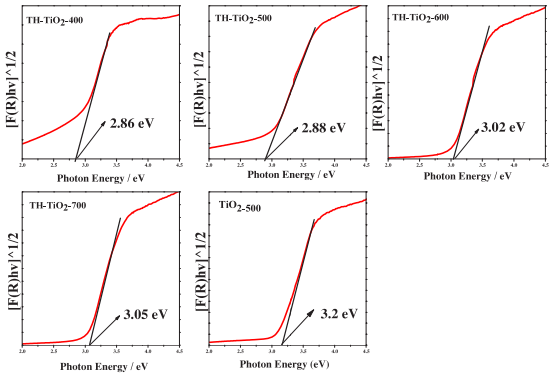

Figure 7. Kubelka-Munk function versus photon energy for band gap estimation

Table 1. Specifications of TH-TiO_{2-a} và TiO_{2-500} materials

Sample	Crystallite size (nm)	Specific surface area (m^2/g)	Band gap energy (eV)
TH-TiO_{2-400}	7.47	73.47	2.86
TH-TiO_{2-500}	9.52	92.25	2.88
TH-TiO_{2-600}	9.79	65.20	3.02
TH-TiO_{2-700}	13.40	47.35	3.05
TiO_{2-500}	14.39	36.01	3.20

3.2. Photocatalytic activities

The tetracycline photocatalytic degradation of TH-TiO_{2-a} and TiO_{2-500} samples is shown in Figure 8. It is worth mentioning that all C, N and S co-doped TiO_2 samples yield a higher photodegradation efficience than the undoped TiO_2 sample. Particularly, the TH-TiO_{2-500} show the best photocatalytic activity under the visible light irradiation (96%). This is because the TH-TiO_{2-500} sample has the largest specific surface area and thereby having more active sites for the adsorption and decomposition of the tetracycline.

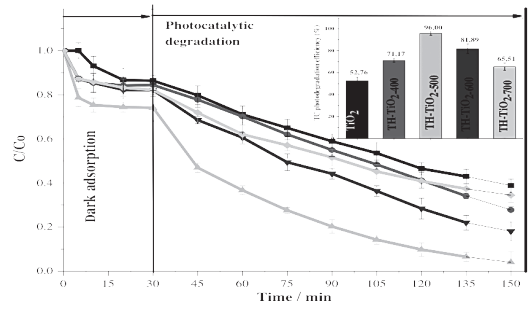

Figure 8. The change in C/Co as a function of time for TiO_{2-500} và TH-TiO_{2-a} (a = 400, 500, 600 and 700°C), tetracycline concentration of 30 mg/L

4. CONCLUSIONS

C, N and S co-doped TiO_2 photocatalysts prepared by the hydrothermal method were characterized by modern physical methods. The effect of the annealing temperature on the tetracycline photodegradation of the TH-TiO_{2-a} samples was systematically investigated. Experimental results indicate that the annealing temperature has a great influence on the particle size and band gap energy and thereby affecting the photocatalytic activities of the TH-TiO_{2-a} samples. It is found that all co-doped samples show the high photocatalytic performance in the visble light region. This suggests that (C, N, S) co-doped TiO_2 photocatalysts are promising candidates for the photocatalytic decomposition of toxic organic substances in the wastewater under the visible light irradiation.

Acknowlegment: *This research is partly funded by the TEAM project (ZEIN2016PR431 code).*

REFERENCES

1. X. Chen and S. S. Mao. Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications, *Chemical reviews,* **2007,** *107* (7), 2891-2959.
2. A. Molea, V. Popescu, N. A. Rowson and A. M. Dinescu. Influence of pH on the formulation of TiO_2 nano-crystalline powders with high photocatalytic activity, *Powder technology,* **2014,** *253,* 22-28.
3. F. Li, H. Li, L.-x. Guan and M.-m. Yao. Nanocrystalline Co^{2+}/F^- codoped TiO_2–SiO_2 composite films for environmental applications, *Chemical Engineering Journal,* **2014,** *252,*1-10.
4. H. H. Tseng, W. W. Lee, M.-C. Wei, B.-S. Huang, M.-C. Hsieh and P.-Y. Cheng. Synthesis of TiO_2/SBA-15 photocatalyst for the azo dye decolorization through the polyol method, *Chemical Engineering Journal,* **2012,** *210*, 529-538.
5. A. Molea, V. Popescu and N. A. Rowson. Effects of I-doping content on the structural, optical and photocatalytic activity of TiO_2 nanocrystalline powders, *Powder technology,* **2012,** *230,* 203-211.
6. L. Xiao, J. Zhang, Y. Cong, B. Tian, F. Chen and M. Anpo. Synergistic effects of doped Fe^{3+} and deposited Au on improving the photocatalytic activity of TiO_2, *Catalysis letters,* **2006,** *111* (3-4), 207-211.
7. P. N. Kapoor, S. Uma, S. Rodriguez and K. J. Klabunde. Aerogel processing of MTi_2O_5 (M = Mg, Mn, Fe, Co, Zn, Sn) compositions using single source precursors: Synthesis, characterization and photocatalytic behavior, *J. Mol. Catal. A Chem,* **2005,** *229* (1-2), 145–150.
8. T. V. Sviridova, L. Y. Sadovskaya, E. Shchukina, A. Logvinovich, D. Shchukin and D. Sviridov. Nanoengineered thin-film TiO_2/h-MoO_3 photocatalysts capable to accumulate photoinduced charge, *Journal of Photochemistry and Photobiology A: Chemistry,* **2016,** *327,* 44-50.
9. M. Sabarinathan, S. Harish, J. Archana, M. Navaneethan, H. Ikeda and Y. Hayakawa. Highly efficient visible-light photocatalytic activity of MoS_2–TiO_2 mixtures hybrid photocatalyst and functional properties, *RSC Advances,* **2017,** *7* (40), 24754-24763.
10. H. Liu, Y. Wu and J. Zhang. A new approach toward carbon-modified vanadium-doped titanium dioxide photocatalysts, *ACS applied materials & interfaces,* **2011,** *3* (5), 1757-1764.
11. G. Zhang, Y. C. Zhang, M. Nadagouda, C. Han, K. O'Shea, S. M. El-Sheikh, A. A. Ismail and D. D. Dionysiou. Visible light-sensitized S, N and C co-doped polymorphic TiO_2 for photocatalytic destruction of microcystin-LR, *Applied Catalysis B: Environmental,* **2014,** *144,* 614-621.
12. S. Wahyuningsih, A. H. Ramelan, R. M. I. Munifa, L. N. M. Z. Saputri and U. Chasanah. Synthesis of TiO_2 nanorods from titania and titanyl sulfate produced from Ilmenite dissolution by hydrothermal method, *Journal of Physics: Conference Series,* **2016,** *776.*
13. Lan Nguyen Thi, Anh Vo Hoang, An Hoang Duc, Hung Nguyen Phi, Nhiem Dao Ngoc,

Van Thang Bui, Lieu Pham Khac and Khieu Dinh Quang. Synthesis of CNS-Tridoped TiO_2 from Vietnam Ilmenite Ore and Its Visible Light-Driven-Photocatalytic Activity for Tetracyline Degradation, *Journal of Nanomaterials,* **2020,** *2020,*1-14.

14. M. Wu, B. Yang, Y. Lv, Z. Fu, J. Xu, T. Guo and Y. Zhao. Efficient one-pot synthesis of Ag nanoparticles loaded on N-doped multiphase TiO_2 hollow nanorod arrays with enhanced photocatalytic activity, *Applied Surface Science,* **2010,** *256* (23), 7125-7130.

15. H. Zhang, Z. Xing, Y. Zhang, Z. Li, X. Wu, C. Liu, Q. Zhu and W. Zhou. Ni^{2+} and Ti^{3+} co-doped porous black anatase TiO_2 with unprecedented-high visible-light-driven photocatalytic degradation performance, *RSC Advances,* **2015,** *5* (129), 107150-107157.

16. M. A. Mohamed, W. Salleh, J. Jaafar, A. Ismail and N. A. M. Nor. Photodegradation of phenol by N-Doped TiO_2 anatase/rutile nanorods assembled microsphere under UV and visible light irradiation, *Materials Chemistry and Physics,* **2015,** *162,* 113-123.

17. Y. K. Chen, Y. F. Lin, Z. W. Peng and J. L. Lin. Transmission FT-IR study on the adsorption and reactions of lactic acid and poly (lactic acid) on TiO_2, *The Journal of Physical Chemistry C,* **2010,** *114* (41), 17720-17727.

18. Y. Li, C. Xie, S. Peng, G. Lu and S. Li. Eosin Y-sensitized nitrogen-doped TiO_2 for efficient visible light photocatalytic hydrogen evolution, *Journal of Molecular Catalysis A: Chemical,* **2008,** *282* (1-2), 117-123.

19. G. Zhang, Y. C. Zhang, M. Nadagouda, C. Han, K. O'Shea, S. M. El-Sheikh, A. A. Ismail and D. D. Dionysiou. Visible light-sensitized S, N and C co-doped polymorphic TiO_2 for photocatalytic destruction of microcystin-LR, *Applied Catalysis B: Environmental,* **2014,** *144,* 614-621.

20. N. Yao, C. Wu, L. Jia, S. Han, B. Chi, J. Pu and L. Jian. Simple synthesis and characterization of mesoporous (N, S)-codoped TiO_2 with enhanced visible-light photocatalytic activity, *Ceramics International,* **2012,** *38* (2), 1671-1675.

21. C. Han, M. Pelaez, V. Likodimos, A. G. Kontos, P. Falaras, K. O'Shea and D. D. Dionysiou. Innovative visible light-activated sulfur doped TiO_2 films for water treatment, *Applied Catalysis B: Environmental,* **2011,** *107* (1-2), 77-87.

22. R. Venkatkarthick, D. J. Davidson, S. Vasudevan, G. Sozhan and S. Ravichandran. An Investigation of Interfacial and Photoelectrochemical Performance of Thermally Prepared C, N -codoped TiO_2 Photoanodes for Water Splitting, *Chemistry Select,* **2017,** *2* (1), 288-294.

23. X. Y. Zhang and X. L. Cui. Preparation and photocatalytic hydrogen evolution performance of C, N co-doped nano TiO_2 photocatalysts, *Acta Physico-Chimica Sinica,* **2009,** *25* (9), 1829-1834.

24. J. Geng, D. Yang, J. Zhu, D. Chen and Z. Jiang. Nitrogen-doped TiO_2 nanotubes with enhanced photocatalytic activity synthesized by a facile wet chemistry method, *Materials Research Bulletin,* **2009,** *44* (1), 146-150.

25. M. Primet, P. Pichat and M. V. Mathieu. Infrared study of the surface of titanium dioxides. I. Hydroxyl groups, *The Journal of Physical Chemistry,* **1971,** *75* (9), 1216-1220.

26. X. F. Lei, X. X. Xue, H. Yang, C. Chen, X. Li, M. C. Niu, X. Y. Gao and Y. T. Yang. Effect of calcination temperature on the structure and visible-light photocatalytic activities of (N, S and C) co-doped TiO_2 nano-materials, *Applied Surface Science,* **2015,** *332,* 172-180.

27. J. Lv, T. Sheng, L. Su, G. Xu, D. Wang, Z. Zheng and Y. Wu. N, S co-doped-TiO_2/fly ash beads composite material and visible light photocatalytic activity, *Applied Surface Science,* **2013,** *284,* 229-234.

28. M. Khan, J. Xu, N. Chen and W. Cao. First principle calculations of the electronic and optical properties of pure and (Mo, N) co-doped anatase TiO_2, *Journal of Alloys and Compounds,* **2012,** *513,* 539-545.

29. O. Carp, C. L. Huisman and A. Reller. Photoinduced reactivity of titanium dioxide, *Progress in solid state chemistry,* **2004,** *32* (1-2), 33-177.

30. T. Matsumoto, N. Iyi, Y. Kaneko, K. Kitamura, S. Ishihara, Y. Takasu and Y. Murakami. High visible-light photocatalytic activity of nitrogen-doped titania prepared from layered titania/ isostearate nanocomposite, *Catalysis today,* **2007,** *120* (2), 226-232.

31. F. Dong, W. Zhao and Z. Wu. Characterization and photocatalytic activities of C, N and S co-doped TiO_2 with 1D nanostructure prepared by the nano-confinement effect, *Nanotechnology,* **2008,** *19*(36), 365-607.

32. Y. L. Kuo, T. L. Su, F. C. Kung and T. J. Wu. A study of parameter setting and characterization of visible-light driven nitrogen-modified commercial TiO_2 photocatalysts, *Journal of hazardous materials,* **2011,** *190* (1-3), 938-944.