EXAMINING THE PHASE COMPOSITION OF TiO_2 NANOPARTICLES DERIVED FROM SOL-GEL: IMPACT OF REACTION AND PROCESSING CONDITIONS

Van Thuy Vu[1], Van Manh Nguyen[2], Viet Thu Tran[1,*]

[1]*Faculty of Physics and Chemical Engineering, Le Quy Don Technical University, Hanoi, Vietnam*

[2]*Faculty of Chemical Technology, Hanoi University of Industry*

Abstract

TiO_2 nanoparticles with crystallite size less than 15 nm were prepared from $TiCl_4$ precursor by a modified sol-gel route. As-prepared TiO_2 nanoparticles were extensively characterized using X-ray diffractometry, and their crystallite size was calculated using Debye-Scherrer formula. The phase composition and crystallite size of TiO_2 nanoparticles were dependent on reaction parameters including $TiCl_4$ concentration, reaction temperature, annealing temperature, and surfactant. The crystallite size increases with increasing annealing temperature. Amorphous-anatase phase transition occurs at 400 - 450°C and anatase-rutile phase transition occurs at ca. 700°C.

Keywords: *TiO_2 nanoparticles; sol-gel; anatase; rutile; crystal structure.*

1. Introduction

In recent decades, TiO_2 nanomaterials have attracted numerous research and development efforts due to its exceptional optical, physical and chemical properties [1, 2]. Among their various allotropes [3], TiO_2 in anatase and rutile phases has received the most interest due to their photocatalytic properties and superhydrophilicity, which endose them to be used in photocatalytic processes, including decomposition of organic compounds, sterilization, and CO_2 reduction [1, 4]. It has been widely known that phase composition and particle size are among most important factors determining properties and applications of TiO_2 nanomaterials [5-8].

TiO_2 nanoparticles (NPs) can be conveniently prepared by solution routes [9]. Among them, hydrolysis of inorganic or organometallic salts of titanium such as $TiCl_4$ is conveniently used as initial step in the production of TiO_2 [10, 11]. The hydrolysis of $TiCl_4$ have been performed at zero temperature for long time (24 hours) [12], at

[*] Email: tranvietthu@lqdtu.edu.vn

DOI: 10.56651/lqdtu.jst.v1.n02.715.pce

80 - 100^{o}C (6 - 12 hrs) [13], or at higher temperature (150 - 180^{o}C) [1], all of these routes require temperature-modulating equipments. In this work, we prepared TiO_2 NPs by the hydrolysis of $TiCl_4$ precursor in ethanol/water mixture solvent in the presence of ammonia, followed by drying and heating at various reaction and processing conditions. We found that the hydrolysis of $TiCl_4$ can be simply performed at room temperature without the need of heating or cooling. We further explored the effect of various parameters on phase composition and crystallite size, including annealing temperature, heating temperature, $TiCl_4$ concentration, hydrolyzing temperature, and the type of surfactants used.

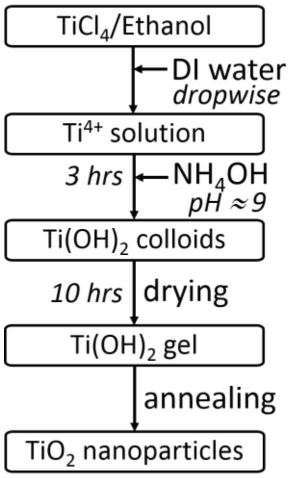
2. Methodology

2.1. Chemicals

Titanium(IV) chloride ($TiCl_4$) was purcharsed from Mercks. Ammonia solution 25% (NH_4OH), ethanol (C_2H_5OH), sodium dodecyl sulfate (SDS), and triethanolamine (TEA) were purchased from Xilong Scientific Co., Ltd.

2.2. Preparation of TiO_2 NPs

The synthesis of TiO_2 NPs was demonstrated in Scheme 1. $TiCl_4$ was dissolved in C_2H_5OH with predefined amount at room temperature under vigorous stirring. To achieve desired concentration of $TiCl_4$, DI water was dropped into the reaction system under steady stirring (300 rpm). After 30 min, ammonia solution was dropped into the system to induce precipitation of $Ti(OH)_2$ and pH was maintained at ~9. After 3 hrs, $Ti(OH)_2$ gel was obtained by centrifugating the precipitates and repeated washing using distilled water. The gel was dried for 10 hrs and annealed in a furnace in air. To investigate the effect of annealing temperature, $Ti(OH)_2$ sol was dried at 120^{o}C, then annealed at different temperatures (400, 450, 500, 600, 700 and 800^{o}C) and durations (1 or 2 hrs). To investigate the effect of drying temperature, $Ti(OH)_2$ sol was dried at different temperatures (100, 120, 140, and 160^{o}C), then annealed at 400^{o}C for 2 hrs. To investigate the effect of $TiCl_4$ concentration, the hydrolysis was performed at five different values of $TiCl_4$ concentration (0.025; 0.05; 0.1; 0.2; and 0.4 mol.L^{-1}), and the resulting $Ti(OH)_2$ sol were dried at 120^{o}C and annealed at 400^{o}C for 2 hrs. To investigate the effect of hydrolyzing temperature, we carried out the hydrolysis at different temperatures (room temperature ~25^{o}C, 40, 60, and 80^{o}C), then $Ti(OH)_2$ sol were also dried at 120^{o}C and annealed at 400^{o}C for 2 hrs.



Scheme 1. Scheme for the synthesis of TiO_2 NPs.

2.3. Characterization

XRD studies were performed on SIEMEN D5005 diffractometer equipped with Cu anode, scanning angle 10 - 70°, scanning rate 0.030°/sec. Characteristic XRD patterns were used to determine phase composition. In the current study, the average crystallite size (*r*, in nm) of TiO_2 nanoparticles was calculated by applying Debye-Scherrer formula to (110) diffraction peak, the one with the highest intensity among the patterns [14]:

$$r = \frac{k\lambda}{\beta\cos\theta}$$

whereas k is a constant (k = 0.9 for nearly sphere particles); λ is wavelength of CuKα irradiation, λ = 0.154056 nm; β is full width at half maximum of characteristic peak in XRD patterns, calculated according to Gauss or Voigt function in radian; 2θ is diffraction peak corresponding to maximum of the characteristic pattern. TEM images were obtained on a JEOL JEM 1010 microscope under an acceleration voltage of 80 kV.

3. Results and discussion

3.1. Effect of annealing temperature

XRD patterns of samples obtained at different annealing temperatures are shown in Fig. 1. Upon annealing sample at 400^{o}C for 1 hour, the sample remains amorphous as no clearly defined XRD patterns were observed. As annealing time was prolonged to 2 hour, the transition of amorphous TiO_2 to anatase phase occurred. In the temperature range from 400 to 600^{o}C, only anatase phase is formed. In addition, crystallite size of anatase phase dramatically increases with the annealing temperature, from 10.5 nm (at 400^o) to 21.5 nm (at 600°C). At 600°C, phase transisition from anatase to rutile starts to occur although not very clearly. When annealing temperature is 700°C, the phase transition obviously occurs, and average crystallite size quickly increases. As a result, the mass ratio of rutile/anatase increases. Phase transition from anatase to rutile completes at 800°C with the only phase was noticed is rutile.

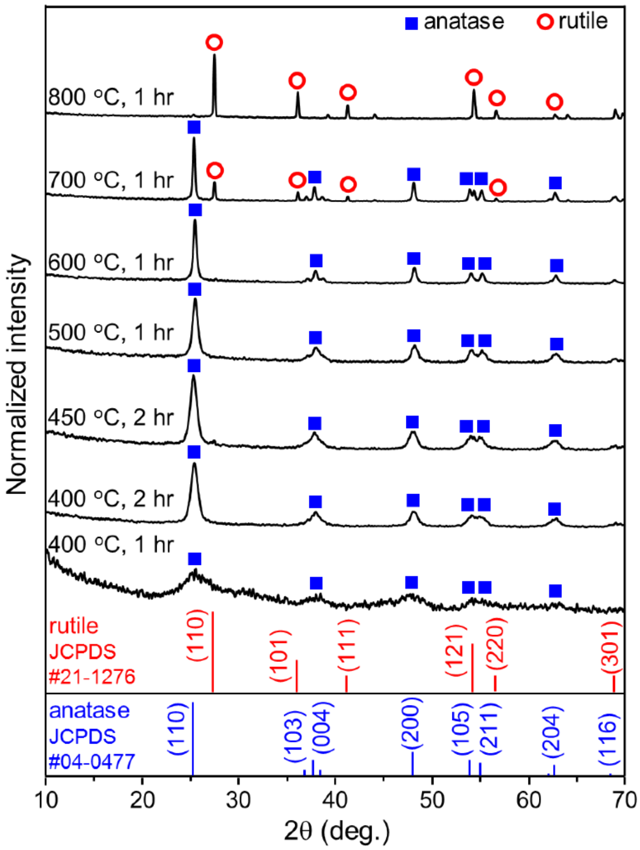


Fig. 1. XRD patterns of TiO_2 NPs obtained at different annealing temperatures.

Figure 2 shows the dependence of crystallite size of as-prepared TiO_2 particles on annealing temperature. The crystallite size of as-prepared TiO_2 NPs proportionally increases with annealing temperature, from 10.5 nm (at 400°C) to 59.3 nm (at 800°C). Crystallite size slowly increases at lower range of annealing temperature (400, 450 and 500°C), and more gradually at higher range of temperature (600, 700 and 800°C). This trend is similar to previously reported result [15], and can be explained as following. When annealing temperature is high, activation energy is low, and thus growth rate is high. In contrast, when annealing temperature is low, activation energy is very high, and thus growth rate is small.

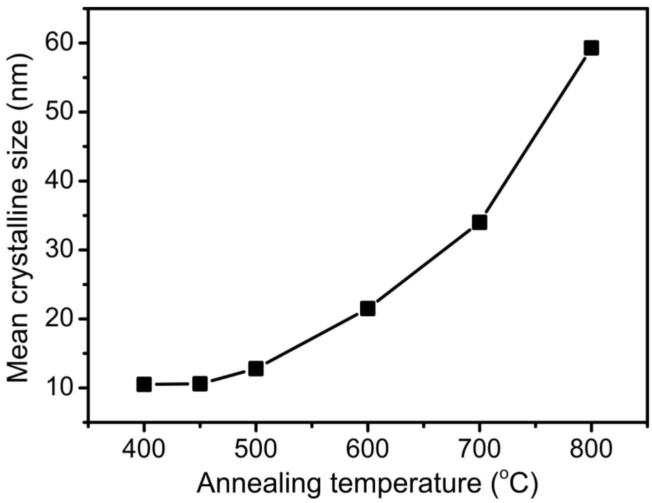


Fig. 2. Crystallite size of as-prepared TiO_2 NPs as a function of annealing temperature.

3.2. Effect of drying temperature

XRD patterns and average crystallite size of as-prepared TiO_2 NPs obtained at different drying temperatures are shown in Fig. 3 and Fig. 4, respectively. Varying drying temperature results in TiO_2 NPs having diameter from 10.5 to 13.1 nm. Drying the $Ti(OH)_2$ gel at 120°C results in TiO_2 NPs with smallest diameter (10.5 nm). At smaller temperature (100°C), absorbed water might be not completely eliminated and thus affecting the nucleation and growth of TiO_2 crystallines in subsequent annealing process. Contrarily, drying the $Ti(OH)_2$ gel at higher temperatures (140 and 160°C) might result in the aggregation and agglomeration of TiO_2 sols, causing the crystallite size to increase.

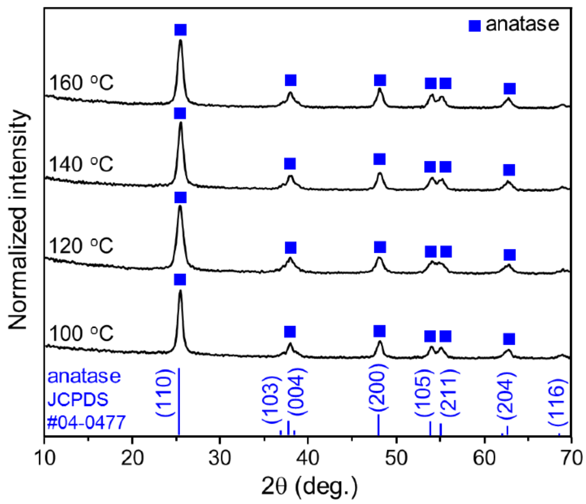


Fig. 3. XRD patterns of as-prepared TiO_2 NPs obtained at different drying temperatures (100, 120, 140, and 160°C).

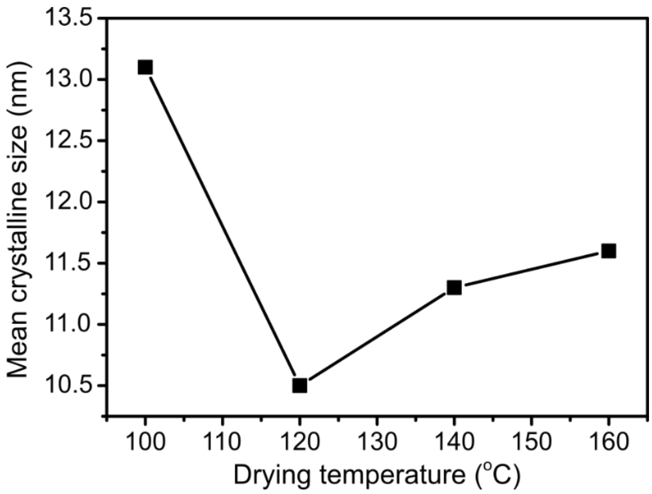


Fig. 4. Crystallite size of as-prepared TiO_2 NPs as a function of drying temperature.

3.3. Effect of $TiCl_4$ concentration

Figure 5 and Figure 6 show XRD patterns and average crystallite size of as-prepared TiO_2 NPs prepared at different concentration of $TiCl_4$, respectively. As observed in Fig. 5, the crystal structure of all samples is anatase without the presence of other phases. Fig. 6 shows that decreasing $TiCl_4$ concentration results in the decrease of TiO_2 particle size, which in our view, can be explained by the suppress of growth rate of TiO_2 NPs, caused by the lack of $TiCl_4$ precursor.

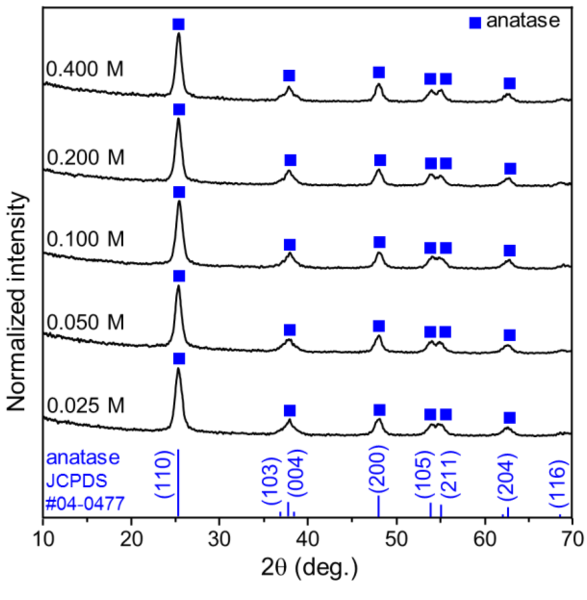


Fig. 5. XRD patterns of as-prepared TiO_2 NPs prepared at different concentration of $TiCl_4$ (0.025, 0.05, 0.1, 0.2, and 0.4 mol.L^{-1}).

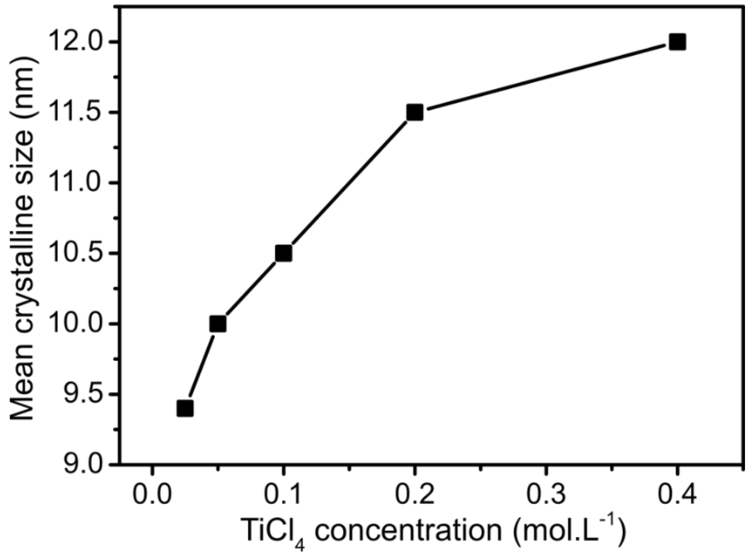


Fig. 6. Crystallite size of as-prepared TiO_2 NPs as a function of $TiCl_4$ concentration.

3.4. Effect of hydrolyzing temperature

Figure 7 and Fig. 8 show XRD patterns and average crystallite size of as-prepared TiO_2 NPs prepared at different hydrolyzing temperatures, respectively. We found that the hydrolyzing temperature plays an important role in the formation of $Ti(OH)_2$ gels. When the hydrolysis was performed at room temperature and slightly above (40 and 60°C), as-obtained TiO_2 NPs were identical and contained only pure-phase of anatase, as shown in Fig. 7. However, at 80°C, $Ti(OH)_2$ gels immediately occurs upon adding DI water into the reaction chamber, indicating fast and strong hydrolysis. More importantly, brookite phase occurs in as-obtained TiO_2. The dependence of crystallite size on hydrolyzing temperature is plotted in Fig. 8, which shows that the crystallite size became smaller at higher hydrolyzing temperature. Perhaps, at higher temperatures hydrolyzing rate is high but the dispersibility of TiO_2 colloids is also high, subsequently the aggregation is efficiently suppressed and crystallite size is decreased. However, at higher temperatures (60 and 80°C) the difference in crystallite size is quite small.

TEM images (Fig. 9) shows that TiO_2 particles are basically uniform in shape and size. They are spheres with diameter ranging from 7 to 13 nm. Anatase TiO_2 NPs having smallest size are obtained by annealing at 400°C in 2 hrs.

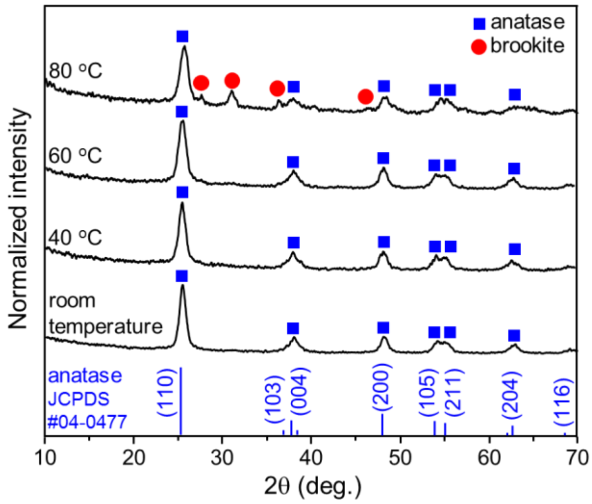


Fig. 7. XRD patterns of TiO_2 samples prepared at different hydrolyzing temperatures.

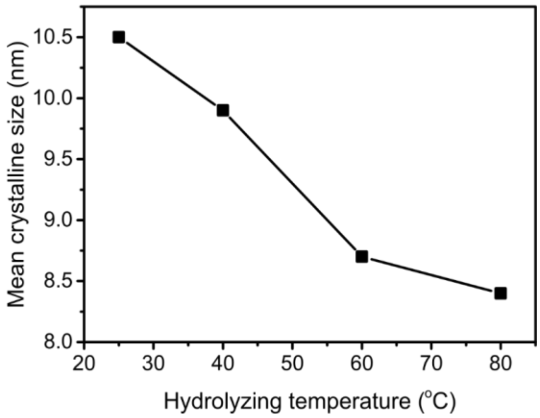


Fig. 8. Crystallite size of as-prepared TiO_2 particles as a function of hydrolyzing temperature.

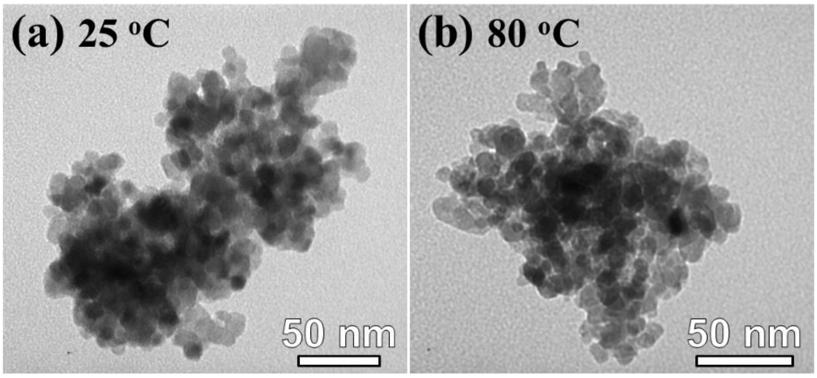


Fig. 9. TEM images of TiO_2 NPs obtained at different hydrolyzing temperature:
(a) Room temperature; (b) 80°C.

3.5. Effect of surfactant

Surfactants are well known to be efficient agents in controlling size and shape of nanomaterials during their nucleation and growth. SDS and TEA have been added to reaction system at both room temperature and 80°C. Controlling experiments were also done without the presence of any surfactants. At room temperature, it seems that the hydrolysis of $TiCl_4$ is not affected by surfactant, as the observed phenomena were the same. However, the crystallite size of TiO_2 is significantly reduced (from 10.5 to 9.1 and 9.6 nm). At at 80°C, both surfactants clearly inhibited the hydrolysis of $TiCl_4$, as we did not observe the immediate formation of precipitation upon adding water. Nevertheless, the crystallite size of TiO_2 is almost same with that of without surfactant. SDS is a little more efficient that TEA.

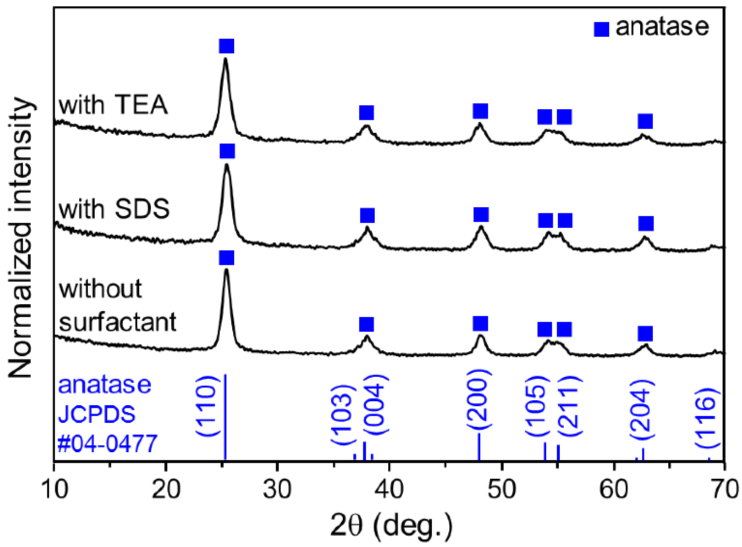


Fig. 10. XRD patterns of TiO_2 NPs prepared without and with surfactants (SDS, TEA).

Table 1. Effect of surfactant to crystallite size of TiO_2 NPs

	Crystallite size	
	Hydrolysis at room temperature	Hydrolysis at 80°C
without surfactant	10.5	8.4
with SDS	9.1	8.6
with TEA	9.6	8.3

4. Conclusions

We have successfully prepared powdered TiO_2 NPs by hydrolysis of $TiCl_4$, followed by drying and annealing at various conditions. The as-prepared TiO_2 NPs have crystallite size less than 15 nm. The phase composition and crystallite size of as-prepared TiO_2 NPs are controllable depending on reaction conditions, whose the most effective factor is annealing temperature. The crystallite size increases with increasing annealing temperature. The other factors are $TiCl_4$ concentration, hydrolyzing temperature, and surfactant. Amorphous-anatase phase transition occurs at 400 - 450^oC and anatase-rutile phase transition occurs at ca. 700^oC. An optimal condition is proposed as following: $TiCl_4$ concentration: 0.1 M; drying at 120^oC in 10 hrs; and annealing at 400^oC in 2 hrs.

References

[1] A. Fujishima, T. N. Rao, D. A. Tryk, "Titanium dioxide photocatalysis," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, Vol. 1 (1), pp. 1-21, 2000. DOI: 10.1016/S1389-5567(00)00002-2

[2] X. Chen, S. S. Mao, "Titanium dioxide nanomaterials: Synthesis, properties, modifications, and applications," *Chem. Rev*, Vol. 107 (7), pp. 2891-2959, 2007. DOI: 10.1021/cr0500535

[3] D. Reyes-Coronado, G. Rodríguez-Gattorno, M. Espinosa-Pesqueira, C. Cab, R. de Coss, G. Oskam, "Phase-pure TiO_2 nanoparticles: anatase, brookite and rutile," *Nanotechnology*, Vol. 19 (14), 2008, 145605. DOI: 10.1088/0957-4484/19/14/145605

[4] Q. D. Truong, T. H. Le, H. T. Hoa, "Amino acid-assisted controlling the shapes of rutile, brookite for enhanced photocatalytic CO_2 reduction," *CrystEngComm*, Vol. 19 (31), pp. 4519-4527, 2017. DOI: 10.1039/C7CE00566K

[5] H. D. Jang, S. K. Kim, S. J. Kim, "Effect of particle size and phase composition of titanium dioxide nanoparticles on the photocatalytic properties," *Journal of Nanoparticle Research*, Vol. 3 (2), pp. 141-147, 2001. DOI: 10.1023/A:1017948330363

[6] J. Panpranot, K. Kontapakdee, P. Praserthdam, "Effect of TiO_2 crystalline phase composition on the physicochemical and catalytic properties of Pd/TiO_2 in selective acetylene hydrogenation," *The Journal of Physical Chemistry B*, Vol. 110 (15), pp. 8019-8024, 2006. DOI: 10.1021/jp057395z

[7] A. Testino, I. R. Bellobono, V. Buscaglia, C. Canevali, M. D'Arienzo, S. Polizzi, R. Scotti, F. Morazzoni, "Optimizing the photocatalytic properties of hydrothermal TiO_2 by the control of phase composition and particle morphology. A systematic approach," *Journal of the American Chemical Society*, Vol. 129 (12), pp. 3564-3575, 2007. DOI: 10.1021/ja067050+

[8] J. T. Carneiro, T. J. Savenije, J. A. Moulijn, G. Mul, "How phase composition influences optoelectronic and photocatalytic properties of TiO_2," *The Journal of Physical Chemistry C*, Vol. 115 (5), pp. 2211-2217, 2011. DOI: 10.1021/jp110190a

[9] S. Gupta, M. Tripathi, "A review on the synthesis of TiO_2 nanoparticles by solution route," *Open Chemistry*, Vol. 10 (2), pp. 279-294, 2012. DOI: 10.2478/s11532-011-0155-y

[10] D. Macwan, P. N. Dave, S. Chaturvedi, "A review on nano-TiO_2 sol-gel type syntheses and its applications," *Journal of Materials Science*, Vol. 46 (11), pp. 3669-3686, 2011. DOI: 10.1007/s10853-011-5378-y

[11] T. H. Wang, A. M. Navarrete-López, S. Li, D. A. Dixon, J. L. Gole, "Hydrolysis of $TiCl_4$: initial steps in the production of TiO_2," *The Journal of Physical Chemistry A*, Vol. 114 (28), pp. 7561-7570, 2010. DOI: 10.1021/jp102020h

[12] M. Šcepanovica, S. Aškrabica, M. Grujic-Brojcina, A. Golubovica, Z. Dohcevic-Mitrovica, A. Kremenovicb, Z. Popovica, "Low-frequency Raman spectroscopy of pure and La-doped TiO_2 nanopowders synthesized by sol-gel method," *Acta physica polonica A*, Vol. 116, pp. 1-4, 2009. DOI: 10.12693/APhysPolA.116.99

[13] S. R. Dhage, V. D. Choube, V. Samuel, V. Ravi, "Synthesis of nanocrystalline TiO_2 at 100°C," *Materials Letters*, Vol. 58 (17), pp. 2310-2313, 2004. DOI: 10.1016/j.matlet.2004.02.021

[14] T. Trung, C. S. Ha, "One-component solution system to prepare nanometric anatase TiO_2," *Materials Science and Engineering: C*, Vol. 24 (1), pp. 19-22, 2004. DOI: 10.1016/j.msec.2003.09.004

[15] B. Li, X. Wang, M. Yan, L. Li, "Preparation and characterization of nano-TiO_2 powder," *Materials Chemistry and Physics*, Vol. 78 (1), pp. 184-188, 2003. DOI: 10.1016/S0254-0584(02)00226-2

ẢNH HƯỞNG CỦA ĐIỀU KIỆN PHẢN ỨNG LÊN THÀNH PHẦN PHA CỦA HẠT NANO TiO_2 CHẾ TẠO BẰNG PHƯƠNG PHÁP SOL-GEL

Vũ Văn Thủy[a], Nguyễn Văn Mạnh[b], Trần Viết Thứ[a]

[a]*Khoa Hóa - Lý kỹ thuật, Trường Đại học Kỹ thuật Lê Quý Đôn*

[b]*Trường Đại học Công nghiệp Hà Nội*

Tóm tắt: Hạt nano TiO_2 có kích thước tinh thể dưới 15 nm được điều chế từ tiền chất $TiCl_4$ bằng phương pháp sol-gel biến tính. Các hạt nano TiO_2 đã điều chế được xác định đặc trưng bằng phép đo nhiễu xạ tia X và kích thước tinh thể của chúng được tính toán bằng công thức Debye-Scherrer. Thành phần pha và kích thước tinh thể của hạt nano TiO_2 phụ thuộc vào các thông số phản ứng bao gồm nồng độ $TiCl_4$, nhiệt độ phản ứng, nhiệt độ ủ và chất hoạt động bề mặt. Kích thước tinh thể tăng khi tăng nhiệt độ ủ. Quá trình chuyển pha vô định hình-anatase xảy ra ở nhiệt độ 400 - 450°C và quá trình chuyển pha anatase-rutil xảy ra ở khoảng nhiệt độ 700°C.

Từ khóa: *Hạt nano TiO_2; sol-gel; anatase; rutil; cấu trúc tinh thể.*

Received: 20/09/2023; Revised: 18/10/2023; Accepted for publication: 17/11/2023

❑