Journal of Metals, Materials and Minerals, Vol.23 No.1 pp.19-24, 2013

Titanium Dioxide Nanostructures Synthesized by Sonochemical – hydrothermal Process

Narongdet WONGPISUTPAISAN[1*], Chokchai KAHATTHA[1,4], Naratip VITTAYAKORN[1,2], Anucha RUANGPHANIT[3], and Wisanu PECHARAPA[1,4]

[1]College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang,Chalongkrung Rd., Ladkrabang Bangkok 10520
[2]Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, 10520
[3]Thai Microelectronics Center, Wangtakien District, AmphurMuang, Chachoengsao, 24000
[4]ThEP Center, CHE, 328 Si Ayutthaya Rd., Bangkok 10400

Abstract

Titanium dioxide particles were prepared by sonochemical–hydrothermal process from a precursor of titanium isopropoxide in the presence of polyvinyl alcohol aqueous solution. Sonication of the precursor was conducted using sonic horn operated at 20 kHz until the completely precipitated product was reached. As-obtained intermediate products were then loaded into a Teflon-lined stainless steel autoclave for hydrothermal process with10M NaOH aqueous solution and heated under different temperature 80-120ºC. The synthesized products were characterized of structural properties and surface morphology by X-ray diffraction spectroscopy and field emission scanning electron microscope. The results show that prepared samples have a good crystallinity and the high purity TiO_2. In addition, it is acknowledged that the hydrothermal temperature has a significant influence on their physical properties.

Keywords: Titanium dioxide particles, Sonochemical, Hydrothermal.

Introduction

In recent years, nanostructure materials have received much attention owing to their superior properties which differ from those of bulk materials. Titanium dioxide (TiO_2) is versatile oxide semiconductor material accompanying its exceptional properties including wide optical band gap (~3.2 eV)[(1)], strong ultraviolet absorptivity, non-toxicity, long-term chemical stability, excellent photocatalysis and high energy conversion efficiency. Applications of TiO_2 have been explored in different fields including photocatalysts[(2)], sensor devices[(3)], solar cell[(4)], antifogging[(5)] and self-cleaning devices[(6)]. Also, there has been a great interest in controlling the structural properties of materials and finding enhanced properties of materials by employing a variety of preparative methods. In addition, many different methods and techniques have been developed for preparation of TiO_2 nanomaterials such as co-precipitation process[(7)], sol-gel process[(8)], electrospinning[(9)], hydrothermal technique[(10)], and sonochemical process.[(11)]

Sonochemical-hydrothermal technique is one of effective techniques for synthesizing a great variety of materials. Sonochemical-hydrothermal synthesis is a prospective method to obtain nanostructures where polymorphism, particle size, crystallinity, morphology, and processing time could be very well controlled as required, comparing to any other techniques. More recently, there have been related works employing the potential of sonochemical-hydrothermal process to synthesize nanostructure of TiO_2. Phan et al. employed a simple hydrothermal process for preparing TiO_2 nanomaterials using concentrated hydrochloric acid[(12)]. Guo et al. reported on the sonochemical synthesis of nanocrystalline TiO_2 by hydrolysis of titanium alkoxides.[(13)] Viana et al. successfully prepared TiO_2 nanoparticles from titanium (IV) isopropoxide diluted in isopropyl alcohol.[(14)]

In this work, we report novel sonochemical -hydrothermal synthesis of titanium dioxide nanostructures via a precursor solution of titanium (IV) isopropoxide. The effects of technique and hydrothermal temperature on their physical properties and microstructure were investigated.

*Corresponding author E-mail: narongdet.wo@gmail.com; E-mail: kpewisan@gmail.com

Materials and Experimental Procedures

10 mL solution of titanium (IV) isopropoxide ($C_{12}H_{28}O_4Ti$, Sigma-Aldrich) in 100 mL deionized water was used as precursor of TiO_2. Sodium hydroxide anhydrous pellets (NaOH, Carlo Erba) and polyvinyl alcohol (PVA, Sigma-Aldrich) which are typically used as general capping template for promoting the anisotropic growth of nanoparticles[15] was added to precursor until pH became 10-12 and stirred for 10 minute. The sonication of solution was performed by a Sonics Model VCX 750 until the completely precipitated product was reached. As-obtained intermediate products were then loaded into a Teflon-lined stainless steel autoclave for hydrothermal process and heated under different temperatures in a range of 80-120ºC for 8 hours. After cooled down to room temperature, the precipitates were washed with deionized water and centrifuged at 5000 rpm for 5 minute. The powders were washed several times until it became neutral. Finally, the as-precipitated powders were dried at 80ºC for about 12 hours. The corresponding diagram of synthesis process in schematically illustrated in Figure 1.

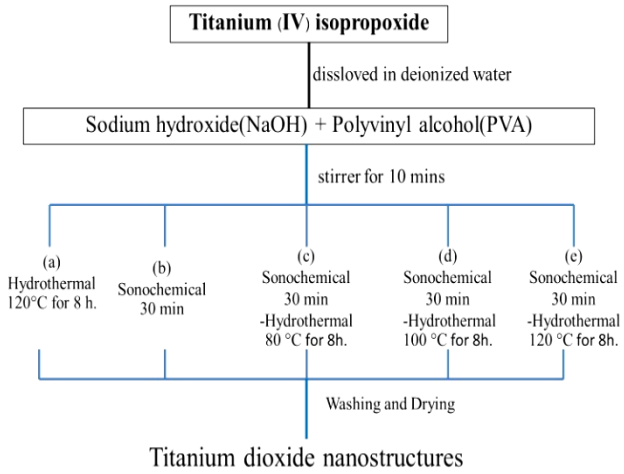

Figure 1. Flow chart of the sonochemical-hydrothermal process.

The powder X-ray diffraction (XRD) patterns of the samples were obtain by PANalytical diffractometer (X'Pert PRO MPD model pw 3040/60) using Cu K_α (λ = 0.154 nm) irradiation at a scanning rate (2θ) of 0.02º s^{-1} and a 2θ range of 10–60º operated at 40 kV and 30 mA. The morphologies of the prepared samples were analyzed using field emission scanning electron microscope (FE-SEM, Hitachi S4700) and transmission electron microscopy (TEM, TECNAI G220). Raman spectra were obtained at room temperature using a Thermo Scientific, The DXR Smart Raman spectrometer, equipped with an InGaAs detector. The radiation from Nd-YAG laser (1.5 W) was used as the excitation source.

Results and Discussion

Figure 2. shows the XRD patterns of TiO_2 nanoparticles (a) hydrothermally operated at 120ºC for 8 hours (b) sonochemical for 30 minute, (c) sonochemical-hydrothermal at 80ºC for 8 hours, (d) sonochemical-hydrothermal at 100ºC for 8 hours and (e) sonochemical-hydrothermal at 120ºC for 8 hours. As seen in Figure 2, all sharp peaks observed in the XRD patterns belong to anatase phase of TiO_2. Noticeable diffraction peaks positioned at 2θ= 25.50°, 37.98°, 48.98° and 54.66° which is observed on the spectra of sonochemical process and sonochemical-hydrothermal process attribute to (101), (004), (103) and (200) orientation plane of anatase-TiO_2.[16] These results indicate that the synthesized powders in monoclinic phase of TiO_2 (TiO_2 (B)) phase can be obtained by single-step hydrothermal process whereas TiO_2 anatase phase was obtained by sonochemical process and double-step sonochemical-hydrothermal process. Possible formation mechanism of TiO_2 undertaken during sonochemical process is represented. During sonication, dissolved titanium isopropoxide in deionized water can undergo hydrolysis and condensation process to create hydrolyzed alcoxides, which have great amount of functional hydroxyl groups. At the same time, rapid collision driven by intense ultrasound energy can generate localized high temperature region, which can expedite the condensation reactions of hydroxyl groups to produce the nucleation of fine spherical TiO_2 nanoparticles. The average crystallite size of TiO_2 can be calculated from the full-width at half maximum (FWHM) by well-known Scherrer's formula expressed in Eq.[1]

$$D = \frac{K\lambda}{\beta \cos\theta}, \qquad (1)$$

Where D is the crystallite size, K is the shape factor, λ is the X-ray wavelength of Cu K_α (0.154 nm), β is the full-width at half maximum (FWHM) and θ is the Bragg angle.[17] The crystallite size of TiO_2 synthesized by each process was calculated from the (101) plane diffraction peak and the corresponding results are shown in Figure 3. It is seen that as-hydrothermally-synthesized product

is in TiO_2 (B) accompanying the characteristic diffraction peak at $2\theta = 29.76°$ and $48.22°$ relating to the result of Yoshida and co-worker.[18] Meanwhile, as-sonochemically-synthesized powder is in anatase phase with average crystallite size of 8 nm. The as-synthesized powder after hydrothermal process shows significant increase in crystallite size up to 10 nm with increasing hydrothermal temperature up to 100°C thereafter slight decreases as the temperature rises to 120°C. This feature may be due to high pressure in hydrothermal process at elevated temperature that can suppress or quench the crystal growth of TiO_2. Moreover, the $Na_2Ti_6O_{13}$ phase also exists in all sonochemical-hydrothermal powders, indicating the typical layered titanate family generated during process with post-thermal treatment.[19]

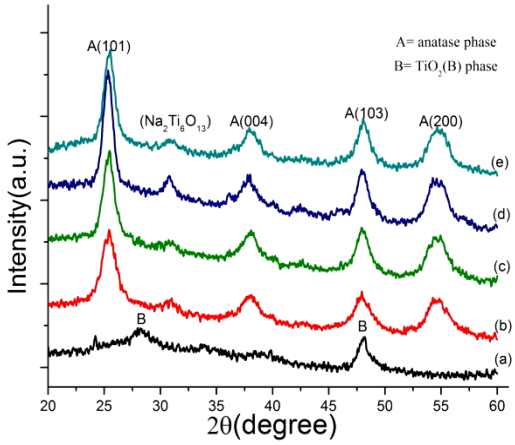

Figure 2. XRD patterns of TiO2 nanoparticles synthesized by (a) hydrothermal at 120ºC, (b) sonochemical for 30 min, (c) sonochemical-hydrothermal at 80ºC, (d) sonochemical-hydrothermal at 100ºC, (e) sonochemical-hydrothermal at 120ºC.

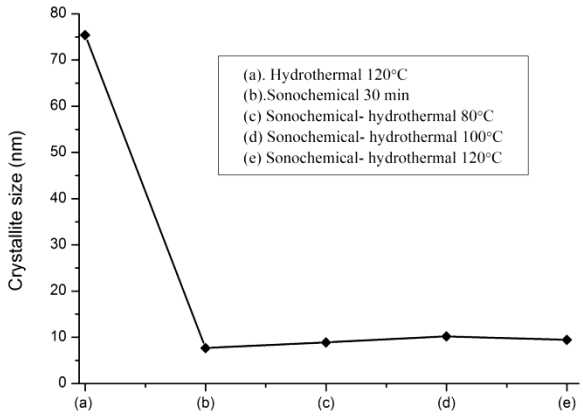

Figure 3. The grain size of TiO_2 synthesized by sonochemical-hydrothermal process.

The morphologies of the as-synthesized products were investigated by FE-SEM. FE-SEM image of TiO_2 obtained by single hydrothermal process and single sonochemical process are shown in Figure 4 (a) and (b), respectively. The nanostructure synthesized by hydrothermal process appears in non-uniform morphology (Figure 4 (a)) meanwhile the product synthesized by sonochemical process exists in spherical morphology (Figure 4(b)). FE-SEM images of the powders obtained by pre-sonochemical process followed hydrothermal process at various temperatures of 80, 100 and 120ºC are shown in Figure 4(c), (d) and (e), respectively. The images disclose the as-synthesized particles have uniformly fine spherical morphology with average size of less than 40 nm.

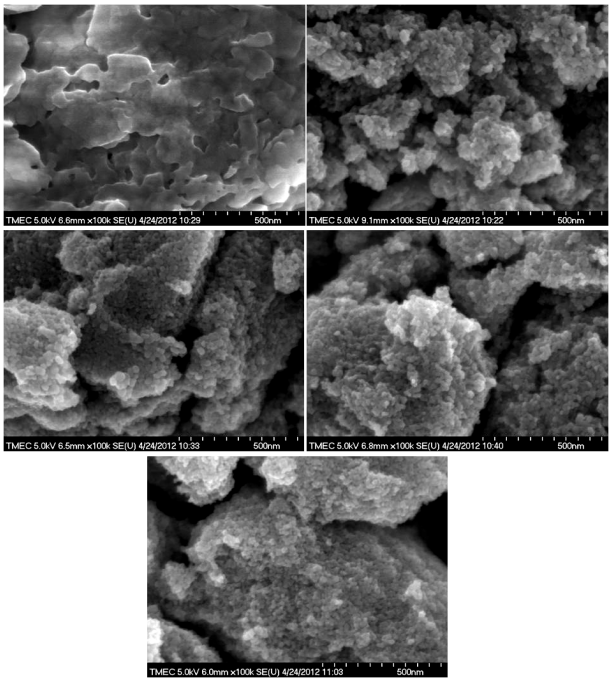

Figure 4. FE-SEM images of TiO_2 nanoparticles synthesized by(a) hydrothermal at 120ºC, (b) sonochemical for 30 min, (c) sonochemical-hydrothermal at 80ºC, (d) sonochemical-hydrothermal at 100ºC, (e) sonochemical-hydrothermal at 120 ºC.

TEM is a useful technique for the analysis of the size and shape of ultrafine particles. Figure. 5 shows the TEM images of TiO_2 nanoparticles (a) hydrothermally operated at 120ºC for 8 hours, (b) sonochemical for 30 minute, (c) sonochemical-hydrothermal at 80ºC for 8 hours, (d) sonochemical-hydrothermal at 100ºC for 8 hours and (e) sonochemical-hydrothermal at 120ºC for 8 hours. The TiO_2 nanostructures grew step by step with considerably different morphology. In the hydrothermal, it is evidently observed that the as-synthesized product

is in uniquely short rod-like structure (Figure 5(a)) with thick wall, corresponding to TiO_2 (B) phase. For single sonochemical process, Figure 5.(b) shows mostly fine distinct shaped particles whose size less than 10 nm. This value monitored by TEM is in good accordance with the result extracted from XRD pattern. The proportion of regular structure and the increase in particle size are attained by the assistance of hydrothermal process with increasing reaction temperature as shown in Figure 5(c-e). The previous XRD results demonstrated that the proportion of the anatase phase is increased via sonochemical-hydrothermal process due to the increase of reaction temperature in system, which is in harmony with the results indicated by TEM images.

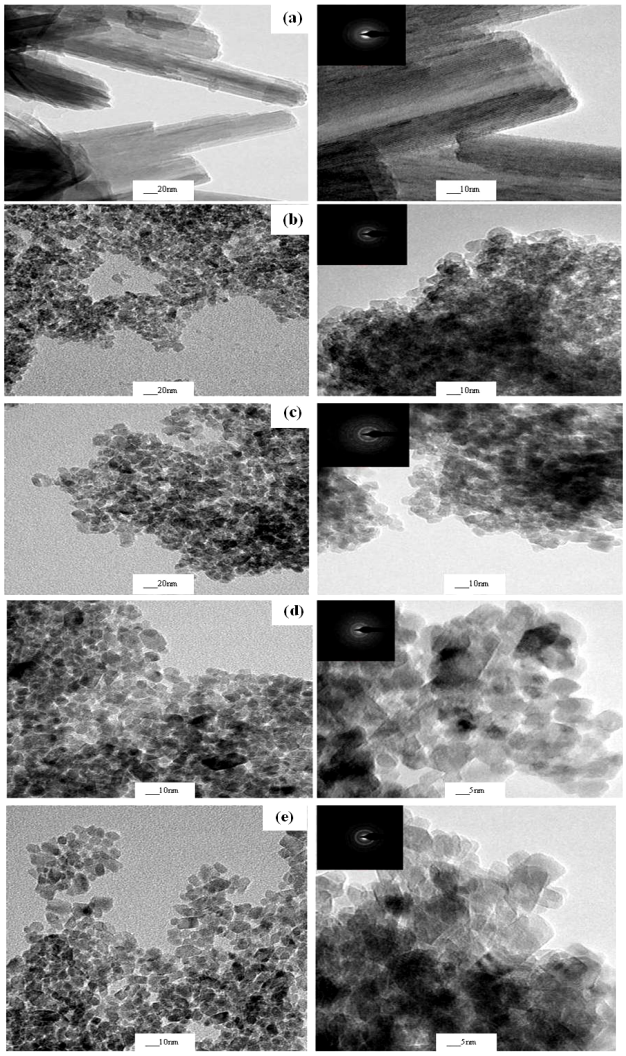

Figure 5. TEM images of TiO2 nanoparticlessynthesized by (a) hydrothermal at 120ºC, (b) sonochemical for 30 minute, (c) sonochemical-hydrothermal at 80ºC, (d) sonochemical- hydrothermal at 100ºC, (e) sonochemical-hydrothermal at 120ºC.

Figure 6. shows the Raman spectra of TiO_2 nanoparticles. Based on factor group analyses, typical anatase has six Raman active modes (A_{1g} + $2B_{1g}$ + $3E_g$). The Raman spectrum of an anatase single crystal has been investigated Choi et al.[20], who concluded that the six allowed modes appeared at 144 cm^{-1} (E_g), 197 cm^{-1} (E_g), 399 cm^{-1} (B_{1g}), 513 cm^{-1} (A_{1g}), 519 cm^{-1} (B_{1g}), and 639 cm^{-1} (E_g). The main spectral feature of sonochemical 30 minutes (b) and sonochemical-hydrothermal 80ºC (C) are closely similar to the reference TiO_2[21]. However, the spectrum of hydrothermal (a), sonochemical-hydrothermal 100ºC (d) and sonochemical-hydrothermal 100ºC (d) show the band broadening with decrease in intensity.

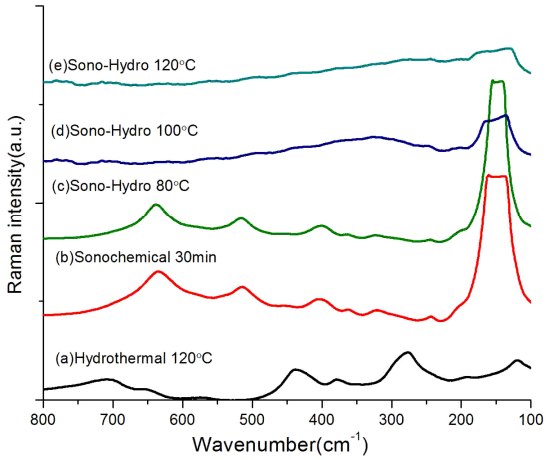

Figure 6. Raman spectra of TiO_2 nanoparticlessynthesized by(a) hydrothermal at 120ºC, (b) sonochemical for 30 minute, (c) sonochemical-hydrothermal at 80ºC, (d) sonochemical- hydrothermal at 100ºC, (e) sonochemical-hydrothermal at 120ºC.

Conclusions

In summary, titanium dioxide nanostructures were synthesized by sonochemical-hydrothermal process starting from a precursor of titanium isopropoxide. Large size of rod-like structures with thick wall of TiO_2 (B) were obtained by single hydrothermal process meanwhile fine nanoparticles of anatase TiO_2 with size less than 10 nm can be obtained by single sonochemical process for 30 minutes. The amelioration in their shape regularity and crystallite size can be achieved by the incorporation of hydrothermal process for short reaction time.

Acknowledgments

This work has partially been supported by National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology,

Thailand, through its program of Center of Excellence Network. Authors gratefully acknowledge the support College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang (KMITL), and Thai Microelectronics Center (TMEC).This work was financially supported by KMITL research fund.

References

1. Isley, S.L., Jordan, D.S. and Penn, R.L. (2009). Titanium dioxide nanoparticles : Impact of increasing ionic strength during synthesis, reflux, and hydrothermal aging. *Mater. Res. Bull*. **44** : 119-125.

2. Hussain, M., Ceccarelli, R., Marchisio,D.L., Fino, D., Russo, N. and Geobaldo, F. (2010). Synthesis, characterization and photocatalytic application of novel TiO_2 Nanoparticles.*Chem. Eng. J.* **157**: 45-51.

3. Boehm, M., Voelklein, F. and Ensinger, W. (2011). Low cost chemical sensor device for supersensitive pentaerythritoltetra - nitrate (PETN) explosives detection based on titanium dioxide nanotubes. *Sensor. Actuat. B.* **158** : 286-291.

4. Zeng, T.W., Lo, H.H., Chang, C.H., Lin, Y.Y., Chen, C.W. and Su, W.F. (2009).Hybrid poly (3-hexylthiophene)/titanium dioxide nanorods material for solar cell applications. *Sol. Energ. Mat. Sol. C.* **93** : 952-957.

5. Law, W.S., Lam, S.W., Gan, W.Y., Scott, J. and Amal, R. (2009). Effect of film thickness and agglomerate size on the superwetting and fog-free characteristics of TiO_2 films. *Thin Solid Films*. **517** : 5425-5430.

6. Jiang, X., Tian, X., Gu, J., Huang, D. and Yang, Y. (2011). Cotton fabric coated with nano TiO_2-acrylate copolymer for photocatalytic self-cleaning by in-situ suspension polymerization. *Appl. Surf. Sci*. **257** : 8451-8456.

7. Zanella, R., Giorgio, S., Shin, C.H., Henry, C.R. and Louis,C. (2004). Characterization and reactivity in CO oxidation of gold nanoparticles supported on TiO_2 prepared by deposition-precipitation with NaOH and urea. *J. Catal*. **222** : 357-367.

8. Prasad, K., Pinjari, D.V., Pandit, A.B. and Mhaske, S.T. (2010). Phase transformation of nanostructured titanium dioxide from anatase-to-rutile via combined ultrasound assisted sol–gel technique. *Ultrason. Sonochem*. **17** : 409-415.

9. Wang, C., Tong, Y., Sun, Z., Xin, Y., Yan, E. and Huang, Z. (2007). Preparation of one-dimensional TiO_2 nanoparticles within polymer fiber matrices by electrospinning. *Mater.Lett*. **61** : 5125-5128.

10. Byrappa, K. and Adschiri, T. (2007). Hydrothermal technology for nanotechnology. *Prog. Cryst. Growth Charact. Mater.* **53** : 117-166.

11. Guo, S., Wu, Z., Wang, H. and Dong, F.(2009). Synthesis of mesoporous TiO_2 nanorods via a mild template-free sonochemical route and their photocatalytic performances. *Catal. Commun.* **10** : 1766-1770.

12. Nguyen Phan, T.D., Pham, H.D., Cuong, T.V., Kim, E.J., Kim, S.W. and Shin, E.W. (2009). A simple hydrothermal preparation of TiO_2 nanomaterials using concentrated hydrochloric acid. *J. Cryst. Growth*. **312**: 79-85.

13. Guo, W., Lin, Z., Wang, X. and Song, G. (2003). Sonochemical synthesis of nanocrystalline TiO_2 by hydrolysis of titanium alkoxides. *Microelectron. Eng*. **66** : 95-101.

14. Viana, M.M., Soares, V.F. and Mohallem, N.D.S. (2010). Synthesis and characterization of TiO_2 nanoparticles. *Ceram. Int*. **36** : 2047-2053.

15. Ranjbar-Karimi, R., Bazmandegan-Shamil, A., Aslani, A. and Kaviani, K. (2010). Sonochemical synthesis, characterization and thermal and optical analysis of CuO nanoparticales. *Physica B.* **405** : 3096-3100.

16. González- Reyes, L., Hernandez-Perez, I., Diaz-BarrigaArceo, L., Dorantes-Rosales, H., Arce-Estrada, E., Suarez-Parra, R. and Cruz-Rivera, J.J. (2010). Temperature effects during Ostwald ripening on structural and bandgap properties of TiO_2 nanoparticles prepared by sonochemical synthesis. *Mat. Sci. Eng. B.* **175** : 9-13.

17. Su, C., Tseng, C.M., Chen, L.F., You, B.H., Hsu, B.C. and Chen, S.S. (2006). Sol–hydrothermal preparation and photocatalysis of titanium dioxide. *Thin Solid Films*. **498** : 259-265.

18. Yoshida, Y., Suzuki, Y. and Yoshikawa, S. (2005). Syntheses of TiO_2(B) nanowires and TiO2 anatase nanowires by hydrothermal and post-heat treatments. *J. Solid. State. Chem.* **178** : 2179-2185.

19. Yu, H., Yu, J., Cheng, B. and Zhou, M. (2006). Effects of hydrothermal post-treatmen on microstructures and morphology of titanate nanoribbons. *J. Solid. State. Chem*. **179** : 349-354.

20. Choi, H.C., Jung, Y.M. and Kim, S.B. (2005). Size effects in the Raman Spectra of TiO_2 nanoparticles. *Vib. Spectrosc*. **37** : 33-38.

21. Šćepanović,M. J., Grujić-Brojčin, M., Dohčević-Mitrović Z.D. and Popović, Z.V. (2009). Characterization of anatase TiO_2 Nano-powder by variable temperature Raman Spectroscopy. *Sci. Sinter*. **41** : 67-73.