

Synthesis of High Performance Titania (TiO₂) Photocatalyst Using Microwave Assisted Synthesis (MAS) Method

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Abstract

In the present research, Microwave Assisted Synthesis(MAS) method is applied to synthesize high performance titania(TiO₂) at 150°C with various heating time. Each prepared titania are characterized by SEM, XRD and N₂ sorption analysis(BET and BJH calculation). This study has shown that the prepared titania by MAS method heated at 150°C with 4 hours treatment has the highest photocatalytic performance compared to the commercial TiO₂ and others titania described in this paper. The titania has effectively reduced Rhodamine B dye up to 96.72% within 90 minutes. This might be due to several factors that improved the catalytic properties of the titania such as high crystallinity of anatase crystalline phase, small crystallite size and high pore volume.

Keywords: TiO₂; microwave assisted synthesis (MAS); BET

1. INTRODUCTION

Heterogeneous photocatalysis has been the subject of numerous investigations as it is an attractive technique for the complete destruction of undesirable contaminants, especially organic dyes in both liquid and gaseous phases by using solar or artificial light illumination. Among of all heterogeneous photocatalyst, titania(TiO_2) has been the practical photocatalyst of choice for a variety of reactions due to its high chemical stability, low cost and non toxic in nature [1]. The photocatalytic activity of titania varies depending on its crystalline phase, crystallinity, surface area, and porosity. Among the common crystalline forms of titania, anatase is generally recognized to be the most active phase as compared to rutile and brookite forms [2,3]. The crystallinity degree of the anatase phase may affect the titania performance [4]. Regarding the surface area, TiO_2 photocatalysis follows the trend of common heterogeneous process, where larger surface area may induce more active sites for the photocatalytic reaction to occur [5]. On the other hand, the sample with high porosity is good for photocatalytic performance [6].

In this study, microwave assisted synthesis(MAS) method is applied to synthesize effective titania due to its short reaction time compare to other methods, such as hydrothermal [1,7-9], sol-gel [10], and soft chemical process [11]. This method requires combination of commercial TiO_2 powder and 10M NaOH aqueous solution which heated rapidly and more uniformly through direct molecular interaction with electromagnetic radiation (absorption of microwaves which are transformed into heat) [9]. The prepared titania are fully characterized by SEM, XRD and N_2 sorption analysis(BET and BJH calculation) before being tested upon degradation of Rhodamine B dye in aqueous solution in order to investigate its potential as a photocatalyst. In this study, the commercial TiO_2 powder was used for comparison.

2. Methodology

2.1 Synthesis of Effective Titania (TiO_2) Photocatalyst

The titania(TiO_2) photocatalyst are synthesized via microwave-assisted synthesis (MAS) method. In typical preparation, 1 g of commercial TiO_2 powder (SIGMA) is suspended in 50 ml of 10 M NaOH aqueous solution in a Teflon vessel. This suspension is ultrasonicated for 30 min at 40°C and the mixture is reacted in a microwave reactor (Milestone Microwave Laboratory Systems) with various heating time ranging from 2 hours to 6 hours at constant temperature(150°C). After that, each sample is washed with 0.1 M HCl solution for an hour, followed by distilled water until pH value became nearly 7. Then, the washed titania is filtered and dried at 60°C overnight. After the titania has been synthesized, each dried titania is calcined in furnace at 450°C for an hour in order to remove impurities as well as to crystallize the titania.

2.2 Characterization

Morphology analysis of the commercial and synthesized TiO₂ powder is examined using scanning electron microscope (SEM, JEOL JSM-6360 LA). An X-ray diffractometer (XRD, Rigaku Miniflex II) with Cu K α radiation ($\lambda=0.15418$ nm) is applied to characterize the crystalline phase of the samples. The samples are spread on a glass slide specimen holder and the scattered intensity is measured between 20° and 80° at a scanning rate of 2 θ =5°/min. Specific surface area for each prepared titania photocatalyst is measured based on Brunauer-Emmett-Teller (BET) multilayer nitrogen gas sorption method (Quantachrome autosorb 1C – Volumetric Technique) at 77.3 K. The pore size and pore volume are estimated using Barrett-Joyner-Halenda (BJH) model. The samples are degassed at 100°C before sorption experiment taking place.

2.3 Photodegradation of Rhodamine B Dye

In this study, each prepared titania is tested to catalyze the degradation of Rhodamine B dye. The photodegradation is carried out inside a homemade photoreactor. Mixture of 100 ml of 10 mg/L dye solution and 0.1 g of synthesized TiO₂ powder is stirred for 10 min in the dark condition so that an adsorption-desorption equilibrium could be established between dye and catalyst surface [9,12]. Then, the mixture solution is irradiated with UV light (302 nm, 15 watt). During the illumination, 5 ml sample solution is withdrawn from the suspension at fixed intervals (30 min) and filtered to separate the catalyst particles. Each collected sample solution is analyzed via UV-Vis spectrophotometer (UV-1601PC, Shimadzu). The same photocatalytic procedure is applied on commercial TiO₂ powder (SIGMA) for comparison.

3. RESULT AND DISCUSSION

3.1 SEM

The SEM technique is carried out in order to investigate the surface morphology of the prepared titania photocatalysts. Figure 1 shows the aggregated of nearly-spherical shape with reasonably uniform size, distributed homogeneously throughout the surface of commercial titania (SIGMA). The precursor powder, thus, consists of typical particulate morphology.

Figure 2 depicts the micrographs of surface morphology of titania prepared by MAS 150°C with various heating time. After treated in MAS 150°C for 2 hours, the titania is agglomerated which formed several large bulky structure. Small packed agglomerates with various shapes and sizes are distributed non-homogeneously on the large bulky surface. When the MAS heating time is prolonged to 4 hours, many elongated structures are formed on the large bulky surface. However, the small packed agglomerates

still exist. As the heating time is kept prolonged to 6 hours, the elongated structure continues to grow and distributed thoroughly on the bulky surface.

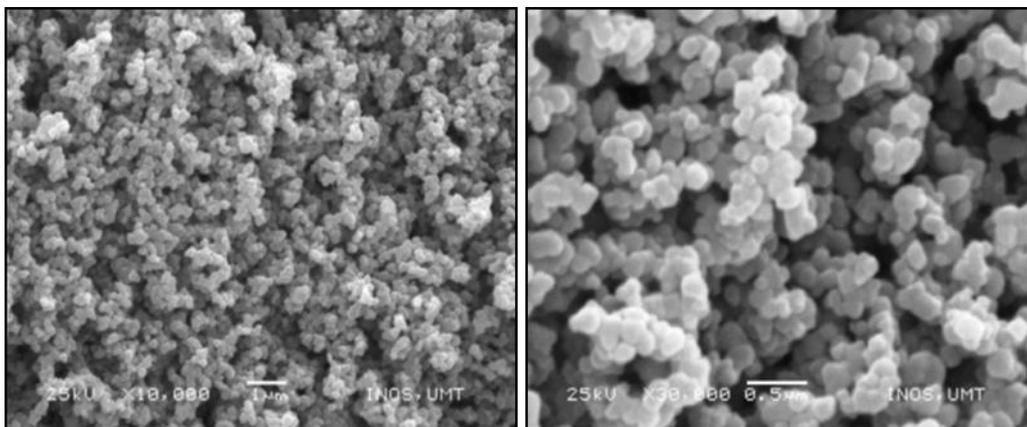


Figure 1: Scanning electron micrographs of commercial titania (SIGMA) with 2 magnification (X10000 and X30000).

3.2 XRD

XRD is applied to determine crystalline phase composition and to estimate crystallite size of the prepared titania photocatalyst. Figure 3 depicted the XRD diffractograms of MAS 150°C with various MAS heating time. From the result, all peaks have been assigned to the anatase crystalline phase (PDF Card No.: 00-021-1272) when the MAS heating time is less than 5 hours. However, the titania with 4 hours treatment shows smoother peaks. This shows that the titania possess high crystallinity. Upon prolonging the MAS heating time to 6 hours, the XRD pattern of the prepared titania comprises two types of peaks which are assigned to sodium titanium oxide ($N_2Ti_6O_{13}$) and anatase (TiO_2) crystalline phase. The existence of $N_2Ti_6O_{13}$ in the lattice structure has deteriorated the crystalline structure of the MAS 6h prepared titania. Meanwhile, the crystalline sizes are obtained using Scherrer's equation [12]:

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

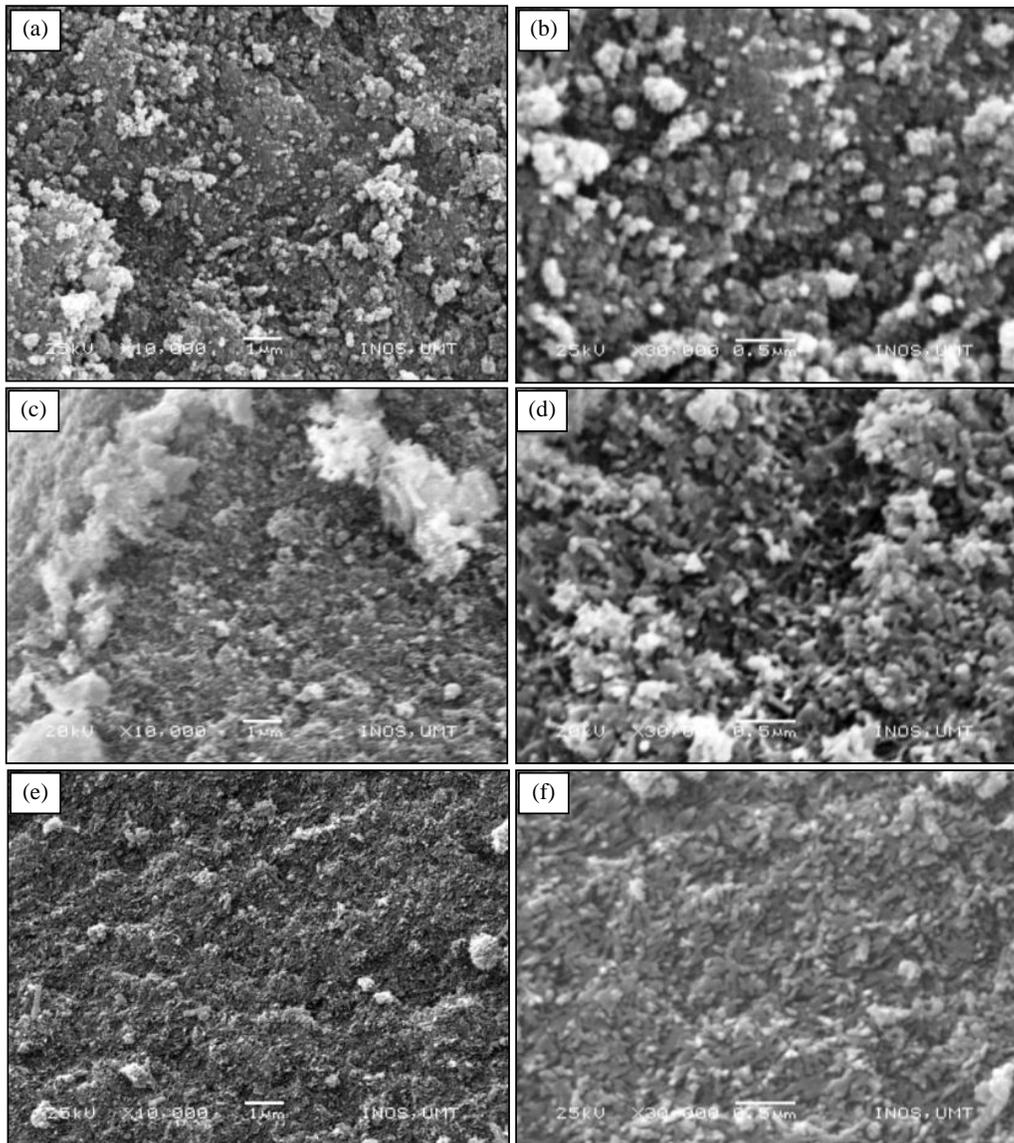


Figure 2: Scanning electron micrographs of titania prepared by MAS treatment at 150°C for 2 hours (A, B), 4 hours (C, D), and 6 hours (E, F) with 2 magnification (X10000 and X30000).

where d is the average crystallite size (nm), λ is the wavelength of Cu $K\alpha$ radiation applied ($\lambda = 0.154$), θ is the Bragg's angle of diffraction, β is the full-width at half maximum intensity (FWHM) of observation at 101 hkl diffraction (converted to radian) and K is the constant (usually applied as ~ 0.94). The crystallite size is decreasing as the MAS heating time is prolonged from 2 hours to 6 hours. The crystalline phase and crystallite size of all the prepared titania has been summarized in Table 1.

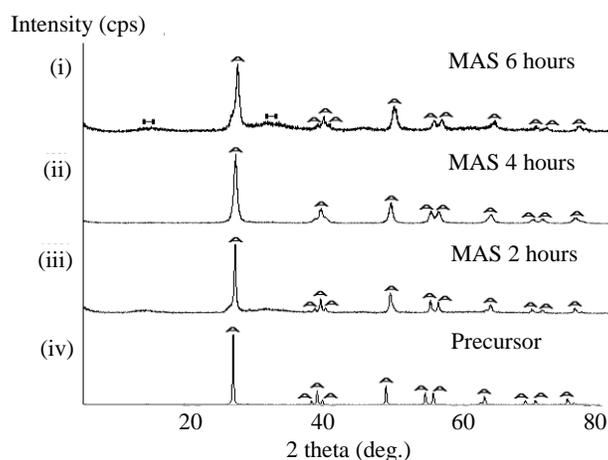


Figure 3: X-ray diffractogram (XRD) patterns of prepared titania by MAS treatment at 150°C for (i) 6 hours, (ii) 4 hours, (iii) 2 hours and subsequently calcined at 450°C for 1 hour, respectively. XRD pattern for (iv) commercial titania(SIGMA) is included for comparison. (A: Anatase (TiO₂); H: Na₂Ti₆O₁₃).

Table 1: Anatase crystallite size for titania prepared via MAS 150°C at various heating time

Type of Photocatalyst	Crystallite size (nm)	Peak assignment
Commercial titania (SIGMA)	43.76	Anatase (TiO ₂)
MAS 150°C 2h	29.90	Anatase (TiO ₂)
MAS 150°C 4h	13.62	Anatase (TiO ₂)
MAS 150°C 6h	8.94	Anatase (TiO ₂) and sodium titanium oxide(N ₂ Ti ₆ O ₁₃)

3.3 N₂ Sorption

Textural characteristics of the samples derived from N₂ sorption analysis are presented in Table 2. The BET total surface area(A_{BET}) and BJH pore diameter(d) of MAS 4h is almost identical with the MAS 2h prepared titania. However, the A_{BET} increased to 139.07 m²/g after MAS 6h treatment. Regardless of A_{BET} increment, the pore size of MAS 150°C 6h titania is almost identical with the 2 hours and 4 hours treated titania, which is 24.77 nm. The commercial titania(SIGMA) has a specific surface area of 39.36 m²/g. However this data is invalid since its BET constant(C) is in negative value. Incorrect incorporation of points during BET plot may be due to the weak energy adsorption of this titania, has contribute to the negative value of C .

Meanwhile, the pore volume of the prepared titania has increased from 0.6670 cm³/g to 0.8254 cm³/g when the treatment time is prolong from 2 hours to 4 hours. However, the pore volume is slightly reduced to 0.7935 cm³/g after MAS 6h treatment.

Figure 4 showed the representative N₂ adsorption–desorption isotherms of the MAS 150°C prepared titania with various heating time. All the titania show similar type IV isotherms, which are representative of mesoporous (pores 2-50 nm in diameter) materials according to the IUPAC classification [13]. Additionally, the loop observed is ascribed to type H3 loop, indicating the presence of mesopores with non-uniform or disordered slit-shaped pores [13]. At the same time, the hysteresis loop approaches P/P₀ = 1, indicating the presence of macropores (pores >50 nm in diameter) in the photocatalyst [13]. As comparison, adsorption capacities of all MAS 150°C prepared titania are much higher than commercial TiO₂ (SIGMA). The results are summarized in Table 3.

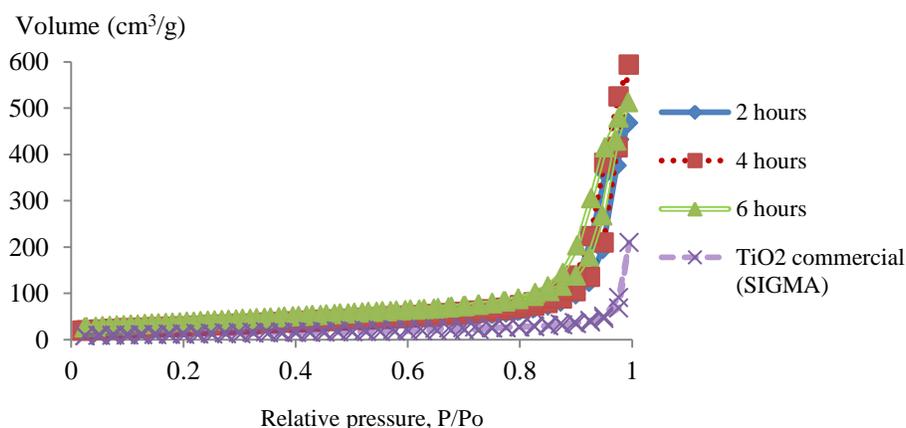


Figure 4: Nitrogen(N₂) adsorption–desorption isotherms plot of MAS 150°C prepared titania with various heating time. TiO₂ commercial(SIGMA) is plotted for comparison.

Table 2: Nitrogen sorption analysis for titania (TiO₂) prepared by MAS 150°C

Type of photocatalyst	A _{BET} (m ² /g)	C	V _p (cm ³ /g)	d (nm)
MAS 150°C 2h	101.99	96.19	0.6670	24.53
MAS 150°C 4h	101.98	137.10	0.8254	24.29
MAS 150°C 6h	139.07	86.38	0.7935	24.77
Commercial titania(SIGMA)	39.36	-3002.00	0.1480	22.43

*A_{BET} = BET total surface area, C = BET constant, V_p = BJH pore volume, d = BJH pore diameter

Table 3: Types of isotherms and porosity for titania(TiO_2) prepared by MAS 150°C

Type of photocatalyst	Type of Isotherms	Type of Hysteresis	Type of Pores	Shape of Pores
MAS 150°C 2h	IV	H3	Mesopore and Macropore	Disordered slit-shaped pores
MAS 150°C 4h	IV	H3	Mesopore and Macropore	Disordered slit-shaped pores
MAS 150°C 6h	IV	H3	Mesopore and Macropore	Disordered slit-shaped pores
Commercial titania(SIGMA)	IV	H3	Mesopore and Macropore	Disordered slit-shaped pores

3.4 Photodegradation of Rhodamine B dye

Titania of MAS 150°C with 4 hours treatment has emerged to be the highest photocatalytic performance with 96.72% of Rhodamine B dye degradation after 90 minutes of UV light irradiation. This result shows significant performance since both of prepared titania at 2 hours and 6 hours possess lower photocatalytic activity. Figure 5 and Table 4 show the graph and total photodegradation percentage of Rhodamine B dye in the presence of titania prepared by MAS 150°C with various heating time.

The highest photocatalytic activity of MAS 4h treated titania is due to small crystallite size(13.62 nm), high crystallinity, and high pore volume($0.8254 \text{ cm}^3/\text{g}$). Although MAS 6h prepared titania possess the smallest crystallite size(8.94 nm) and larger surface area($139.07 \text{ m}^2/\text{g}$), however, its catalytic activity is not effectively performed. This is due to the presence of impurity (sodium titanium oxide) in the prepared titania which has deteriorated its crystalline structure and led to the decreasing of its catalytic activity. The performance of MAS 2 hours prepared titania is even less effective because of larger crystallite size(XRD result) and lower pore volume(BJH result). Thus, there would be fewer active sites where the photogenerated charge carriers could undergo interfacial transfer and react with adsorbed molecules[14].. To our surprise, the MAS 4h prepared titania has better performance in the photodegradation of Rhodamine B, compared to the commercially available titania which approximately 3.96% effective.

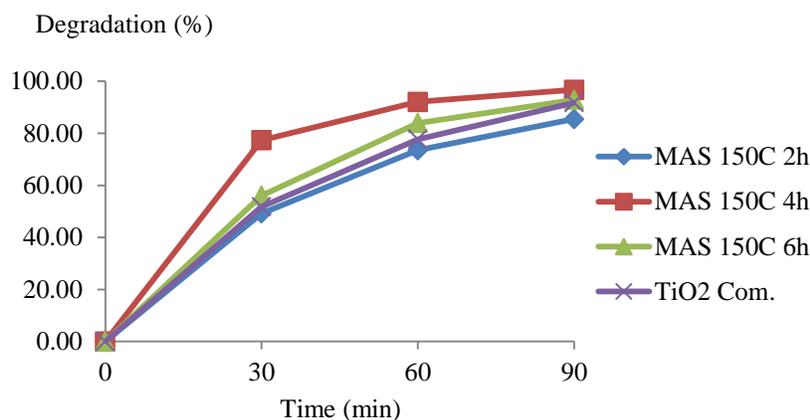


Figure 5: The plot of degradation percentage of 10 ppm Rhodamine B dye against time of UV light irradiation in the presence of MAS 150°C prepared titania with various heating time. Performance of commercial titania(SIGMA) is tested for comparison.

Table 4: Percentage of degradation of Rhodamine B dye catalyzed by MAS 150°C prepared titania with various heating time.

Type of photocatalyst	Percentage(%) of degradation of Rhodamine B dye after 90 minutes
MAS 150°C 2h	85.45
MAS 150°C 4h	96.72
MAS 150°C 6h	92.87
Commercial titania(SIGMA)	91.76

4. CONCLUSION

The Microwave Assisted Synthesis(MAS) technique has produced a potential titania photocatalyst. The titania which is prepared by MAS 150°C of 4 hours treatment has showed the promising performance with almost complete degradation of Rhodamine B dye within a very short time. The high performance of the titania is due to small crystallite size, high crystallinity of anatase crystalline phase, and high pore volume. The titania prepared by MAS method with 4h treatment has higher photocatalytic performance in the degradation of Rhodamine B dye compared to commercial titania(SIGMA).

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REFERENCES

- [1] Sharma, S.D.; Saini, K.K.; Kant, C.; Sharma, C.P. and Jain, S.C. (2008). Photodegradation of dye pollutant under UV light by nano-catalyst doped titania thin films. *Applied Catalysis B: Environmental*, Vol. 84, no.1-2: 233-240, ISSN 0926-3373.
- [2] Machado, N.R.C.F. and Santana, V. S. (2005). Influence of thermal treatment on the structure and photocatalytic activity of TiO₂ P25. *Catalysis Today*, Vol. 107–108: 595-601, ISSN 0920-5861.
- [3] Ou, H.H. and Lo, S.-L. (2007). Review of titania nanotubes synthesized via the hydrothermal treatment: Fabrication, modification, and application. *Separation and Purification Technology*, Vol. 58, no. 1: 179-191, ISSN 1383-5866
- [4] Inagaki, M., Nonaka, R., Tryba, B. and Morawski, A.W. (2006). Dependence of photocatalytic activity of anatase powders on their crystallinity. *Chemosphere*, Vol. 64, no. 3: 437-445, ISSN 0045-6535.
- [5] Gaya, U.B. and Abdullah, A.H. (2008). Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, Vol. 9, no. 1: 1-12, ISSN 1389-5567.
- [6] Guo, B., Shen, H., Shu, K., Zeng, Y. and Ning, W. (2009). The study of the relationship between pore structure and photocatalysis of mesoporous TiO₂. *Journal of Chemical Sciences*, Vol. 121, no. 3: 317-321, ISSN 0974-3626.
- [7] Zhenhua, L., Zhongqing, L., Qingzhi, Y., Yichao, W. and Changchun, G. (2008). Preparation and performance of titanate nanotube by hydrothermal treatment. *Rare Metals*, Vol. 27, no. 2: 187-191, ISSN 1001-0521.
- [8] Zhang, Y.X., Li, G.H., Jin, Y.X., Zhang, Y., Zhang, J. and Zhang, L.D. (2002). Hydrothermal synthesis and photoluminescence of TiO₂ nanowires. *Chemical Physics Letters*, Vol. 365, no. 3-4: 300-304, ISSN 0009-2614.
- [9] Ribbens, S., Meynen, V., Tendeloo, G.V., Ke, X., Mertens, M., Maes, B. U.W., Cool, P. and Vansant, E.F. (2008). Development of photocatalytic efficient Ti-based nanotubes and nanoribbons by conventional and microwave assisted synthesis strategies. *Microporous and Mesoporous Materials*, Vol. 114, no. 1-3: 401-409, ISSN 1387-1811.

- [10] Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T. and Niihara, K. (1998). Formation of titanium oxide nanotube. *Langmuir*, Vol. 14, no.12: 3160-3163, ISSN 0743-7463.
- [11] Qian, L., Du, Z.-L., Yang, S.-Y. and Jin, Z.-S. (2005). Raman study of titania nanotube by soft chemical process. *Journal of Molecular Structure*, Vol. 749, no. 1-3: 103-107, ISSN 0022-2860.
- [12] Asiltürk, M., Sayılkan, F., Erdemoğlu, S., Akarsu, M., Sayılkan, H., Erdemoğlu, M. and Arpaç, E. (2006). Characterization of the hydrothermally synthesized nano-TiO₂ crystallite and the photocatalytic degradation of Rhodamine B. *Journal of Hazardous Materials*, Vol. 129, no. 1-3: 164-170, ISSN 0304-3894.
- [13] Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquérol, J. and Siemieniewska, T. (1985). Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). *Pure and Applied Chemistry*, Vol. 57, no. 4: 603-619, ISSN 0033-4545.
- [14] Dodd, A., McKinley, A., Tsuzuki, T. and Saunders, M. (2007). Optical and photocatalytic properties of nanocrystalline TiO₂ synthesised by solid-state chemical reaction. *Journal of Physics and Chemistry of Solids*, Vol. 68, no. 12: 2341-2348, ISSN 0022-3697.

