

Preparation of nano-crystalline TiO_2
by Sol-gel method using titanium tetraisopropoxide (TTIP)
as a precursor

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Abstract: A sol-gel procedure for producing nano-sized TiO_2 from organometallic precursor -titanium tetraisopropoxide (TTIP), is presented. The characteristic processes and transformations were determined by means of TGA/DTA method. The crystalline structure of the prepared TiO_2 samples was analyzed by means of Raman spectroscopy and XRD method. The size of the crystallites was determined by means of XRD analysis using the Scherrer's equation. In the temperature interval from 250 to 650°C the anatase crystalline structure is stable, while at 650°C the presence of anatase and rutile crystal structures was detected. Increasing the temperature influences the increase of the size of the crystalline particles from 6 nm at 250°C, to more than 100 nm at 800°C.

Key Words: Sol-gel synthesis, TiO_2 , anatase, rutile, crystallite size.

1. Introduction

TiO_2 is a material with wide range of technological applications such as optical devices, sensors, catalysts and photocatalysts etc. [1,2]. In nature, TiO_2 occurs in three forms - rutile, anatase and brookite. The most thermodynamically stable one from them is rutile, whereas brookite and anatase are metastable and transform to rutile on heating [3,4]. Nano-crystalline titanium dioxide materials are a subject of great interest for their improved physical and chemical properties in comparison with its bulk. Because these properties are structure- and size-dependant, it is therefore important to develop new routes of synthesis by which the crystalline structure, the size and the shape of TiO_2 nanocrystals can be readily manipulated. In the recent years, many different methods have been developed and applied for the preparation of nano-sized TiO_2 particles. Methods such as sol-gel [5,6], microemulsion or reverse micelles [7] and hydrothermal synthesis [8] have all been used for the preparation of nano- TiO_2 particles.

Received: July 14, 2012

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In comparison to the other methods, the sol-gel route is considered as very promising one for the synthesis of ultra-fine metallic oxide [9] and has been widely applied for preparing of TiO_2 particles [10]. For synthesis via sol-gel route several different precursors can be used, for example, tetra n-butyl titanate, TiC_{14} and others [11]. The subject of this study is the development and application of a sol-gel procedure for producing nano-sized TiO_2 from organometallic precursor - titanium tetraisopropoxide (TTIP).

2. Experimental

TiO_2 samples were prepared by sol-gel procedure at ambient pressure and temperature of 65°C . As a precursor for preparation of TiO_2 , Ti tetraisopropoxide (TTIP) (Aldrich, 97%) was used. Stirring with $600\div 900$ rpm was applied until fine nano-structured yellow-white powder of $Ti(OH)_4$ was obtained. The produced yellow-white powder after sol-gel procedure was studied by means of TGA/DTA analysis. 20 mg of the studied material were heated in the temperature interval of $25^\circ\text{C}\div 1000^\circ\text{C}$ by heating rate of $10^\circ\text{C min}^{-1}$ in nitrogen atmosphere. The temperatures for the further thermal treatment were chosen according to the characteristic points determined by TGA/DTA analysis (20-30 $^\circ\text{C}$ above the determined points). To decompose $Ti(OH)_4$ to TiO_2 and to remove the residual amount of organic groups, the powder was heated for 2 h in chamber furnace in the air atmosphere at different temperatures. The working temperatures were: 250, 380, 550, 650 and 800°C . In Table 1 the studied samples thermally treated at corresponding temperatures are noted.

Table 1: Notation of the studied TiO_2 samples

Sample	Temperature of thermal treatment, $^\circ\text{C}$
1	250
2	380
3	550
4	650
5	800

Identification of the present structure phases was performed by Raman spectroscopy and X-ray diffraction (XRD). Raman spectra were recorded on micro-Raman multichannel spectrometer Horiba JobinYvon LabRam 300 Infinity. The Raman effect was excited by 632.8 nm laser line from a He:Ne laser. The spectral resolution was set to 4 cm^{-1} . The Raman shift was calibrated using the Raman peak of silica located at 520.7 cm^{-1} . The acquisition time and the accumulation were set to 5 s and 15 scans, respectively. XRD measurements were carried out by X-Ray diffractometer Philips

APD 15, with $CuK\alpha$ radiation. The diffraction data were collected at a constant rate of $0.02^\circ \text{ s}^{-1}$ over an angle range of $2\Theta = 10-90^\circ$. The average crystallite size was calculated from the broadening of the XRD peaks using the Scherrer's equation [12].

3. Results and Discussions

Characteristic curves of the thermal analysis such as TGA and DTA are shown in Fig. 1. The weight losses due to the physico-chemical transformations in $Ti(OH)_4$ during the heating, occurred gradually and exhibit three characteristic points in the TGA curve as shown in Fig.1. The first weight loss below 100°C usually corresponds to physical or chemical desorption of the species such as H_2O (dehydration) and CO_2 (vaporizing of the organic residues in the sample). The main weight loss of about 32 % occurred in the range from 100 to 500°C . The second and the third TGA points correspond to the well defined endothermic peaks in DTA curve (at $162,8^\circ\text{C}$ and $353,4^\circ\text{C}$).

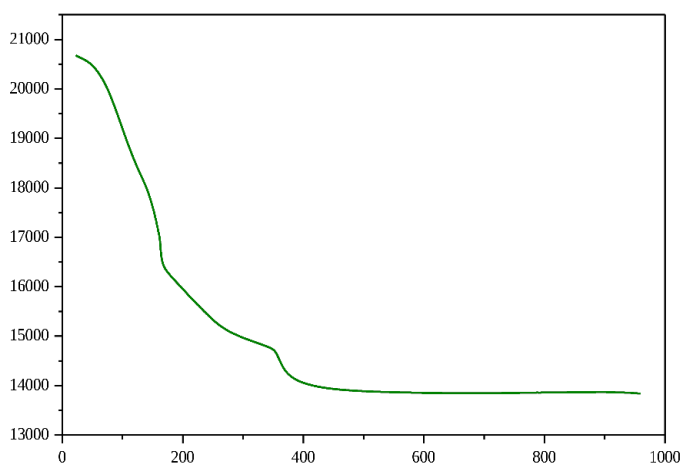


Figure 1: TGA-DTA diagrams of the $Ti(OH)_4$ powder.

The endothermic peak at $95,6^\circ\text{C}$ is due to the evaporation of the physically adsorbed water in the studied samples as result of the air contact. This is in agreement with the literature data [3, 13]. The second point in the range of $162,8^\circ\text{C}$ (DTA) is due to the beginning of the decomposition of the organic residual precursor groups of Ti -tetraisopropoxide. In the range of $220,8^\circ\text{C}$ in DTA curve there is broad maximum with plateau that could be related to the complete decomposition of the organic residues

and start of removal of OH- groups (dehydroxylation) indicating that TiO_2 formation is starting. In order to define precisely this phase transformation, Raman and XRD spectra were recorded and they have confirmed that in this range anatase was found, which is in accordance with literature data [14]. The next exothermic maximum in the range of $353,6^\circ C$ (DTA) without weight loss, suggests complete decomposition of OH- groups (dehydroxylation). Further increase of the temperature contributes to the monotonous decrease of the DTA curve and two characteristic points were detected, at $524,1^\circ C$ and $785^\circ C$. According the Lee et al. [14], above between $450^\circ C$ and $800^\circ C$ transformation of anatase to rutile phase occurs and the difference in the transformation temperature depends on the kind of precursors, the preparation conditions of the particles, and the property of particles. So, these critical points can be correlated with the start of crystalline transformation of anatase to rutile phase [14].

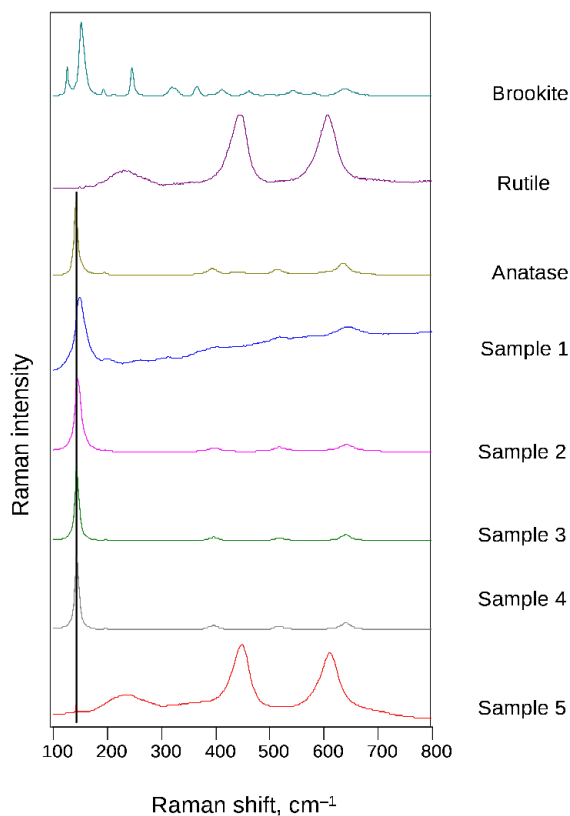


Figure 2: Raman spectra of the produced TiO_2 at different temperatures.

The Raman spectra of the studied samples are presented in Figure 2. For comparison, reference spectra of the characteristic crystalline structures of TiO_2 (brookite,

anatase and rutile) are shown on the top of the diagram. As seen, the spectral view of the samples 2-4 closely resembles to the corresponding spectrum of anatase both for the corresponding band frequency and for peak width. Namely, the smooth baseline as well as the position of each characteristic Raman peaks on the exact same wavenumbers (having the same band width) clearly indicates complete identification of the samples as anatase. On the other hand, the spectral view of the sample denoted as 1, despite the close similarity with the anatase spectrum, shows slight shifting of the bands to higher wavenumbers being especially pronounced for the strongest Raman beak (149.3 cm^{-1} compared to 142.8 cm^{-1}). The sloped and rugged spectrum of the sample 1 points out on its lower crystallinity compared with those treated at higher temperatures [15]. In combination with the band broadening that also took place in the Raman spectrum of sample 1, these changes can be ascribed to the effect of decreasing particle size of the nanoparticles as the temperature of the thermal treatment decreases [16]. Despite the appearance of all the characteristic peaks for rutile in the spectrum denoted as 5, a weak band evolved at 142.8 cm^{-1} . The mentioned peak can be an indicator for subtle presence of anatase in the analyzed, obviously rutile sample, since the reported peak is the strongest one in the Raman spectrum of the latter TiO_2 analogue. But this peak is also corresponds to the multi-photon process characteristic for rutile crystal structure of TiO_2 , i.e. B1g active mode [17, 18]. The nature of this peak can be explained by further XRD analysis.

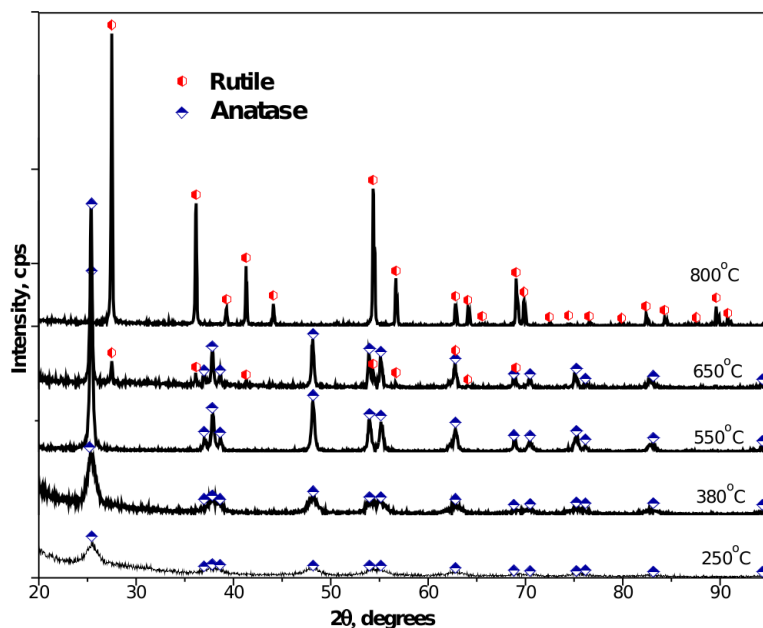


Figure 3: XRD spectra of the produced TiO_2 at different temperatures.

XRD spectra of the studied TiO_2 samples are shown in Fig. 3. XRD spectrum of the sample 1 shows the broadest diffraction peaks with scattered character. This points out on the presence of amorphous TiO_2 . On the other hand, characteristic diffraction peaks for anatase crystalline structure are detected at several positions within this spectrum. So, we can conclude that this sample shows cryptocrystalline structure [19]. According this consideration, the broad maximum with plateau in the range of $220,8^\circ\text{C}$ in DTA curve (222°C DTG curve) except of the complete decomposition of the organic residues, can be ascribed to formation of TiO_2 - amorphous and its further crystallization into anatase. XRD spectrum of the sample 2 is less broad than the previous one and the appeared peaks indicate the presence of anatase. The slight scattered character of spectrum of this sample is an indicator for residual amorphous phase in this sample. Thus, the exothermic peak in the range of $353,6^\circ\text{C}$ (DTA), suggests only complete decomposition of OH- groups (dehydroxylation), but not and complete transformation of cryptocrystalline TiO_2 to anatase. Complete transformation to crystalline anatase occurs at $524,1^\circ\text{C}$ (detected DTA point). XRD spectrum of the sample 3 (treated at 550°C) is well shaped with sharp and narrower peaks characteristic for anatase. Transformation to rutile phase was not detected. The above XRD spectra are in good correlation with the corresponding Raman spectra. The spectrum of the sample 4 treated at 650°C indicates obvious presence of both anatase and rutile phase. The presence of rutile phase was not detected in corresponding Raman spectra. The sample 5 treated at 800°C shows well shaped XRD spectra with peaks characteristic for rutile crystalline form of TiO_2 . Peaks characteristic for anatase were not detected. According to this observation, it is clear that the Raman band of this sample at position 142.9 cm^{-1} corresponds to rutile crystal. Also, we can conclude that at 785°C (DTA detected point) transformation of anatase to rutile is completed. The average crystallite size was calculated from the broadening of the XRD peaks using the Scherrer's equation. The size of the crystallites is shown in Table 2. As the temperature of the thermal treatment increases, the size of the TiO_2 crystallites increases from 6 nm at 250°C to about 100 nm at 800°C .

Table 2: Size of the crystallites of TiO_2 produced at different temperatures

	Temperature of thermal treatment, $^\circ\text{C}$	Diameter of the crystallites, nm
1	250	6
2	380	11
3	550	$35 < d < 45$
4	650	> 45
5	800	> 100

According to the above analysis, we can summarize the detected DTA characteristic

points as is shown in Table 3.

Table 3: The meaning of the characteristic DTA points

DTA, °C	Meaning of the transformation
95.6	Evaporation of the physically adsorbed water in the studied samples as result of the air contact
162.8	Beginning of the decomposition of the organic residual precursor groups of Ti-tetraisopropoxide
220.8	Complete decomposition of the organic residues and start of removal of OH- groups (dehydroxylation) indicating that TiO_2 formation is starting
353.6	Complete decomposition of OH- groups (dehydroxylation)
524.1	Complete transformation to crystalline anatase occurs at 524,1°C
785	Complete transformation of anatase to rutile

4. Conclusions

The main goal of the presented research was to produce nano-structured TiO_2 by sol-gel method in simplified conditions. According to the exposed results and discussions, we could draw the following conclusions:

1. Simplified sol-gel method for preparation of nano-structured TiO_2 was developed using Ti-tetraisopropoxide as a precursor. Sol-gel synthesis was performed at ambient pressure at 68°C. The produced intermediate phase - $Ti(OH)_4$ was thermally treated at different temperatures in air atmosphere in order to produce different crystalline phases of TiO_2 .
2. Decomposition of the organic residual precursor groups of Ti-tetraisopropoxide begins at 162,8°C and fully completed at 220,8°C, while complete decomposition of OH- groups (dehydroxylation) occurs at 353,6°C.
3. As the temperature of the thermal treatment increases, TiO_2 structure changes from cryptocrystalline (anatase and amorphous) above 222°C to completely pure anatase at 524,1°C. Above 650°C there is an existing of two phases - anatase and rutile, while at 785°C transformation of anatase to rutile is completed. Above 785°C pure rutile phase exists.
4. The size of crystallites increases by increasing of temperature in the following order:

6 nm at 250°C, 11 nm at 380°C, 30-45 nm at 550°C, above 45 nm at 650°C and above 100 nm at 800°C. The presented synthesis method offers producing nano-scaled TiO_2 which could be suitable for application as a component for improving the activity of electrocatalysts aimed in hydrogen economy as well as in photocatalysis for degradation of the hazard pollutants that is subject of the further research.

Acknowledgements

This paper has been supported by and carried out within the Project "Synthesis, characterization and application of nano-scaled nonstoichiometric titanium oxides magneli phases" of Ministry of Education and Science of R. Macedonia (Agreement No 13-3576/2, 27.10.2010).

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