PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

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September 22-26, 2014
Belgrade, Serbia

ISBN 978-86-82475-30-9

Title: PHYSICAL CHEMISTRY 2014 (Proceedings)
Editors: Ž. Čupić and S. Anić
Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: "Jovan" Priting and Publishing Company; 200 Copies;
Number of pages: 6+ 441; **Format**: B5; Printing finished in September 2014.

Text an Layout: "Jovan"

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12th International Conference on
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Organized by
The Society of Physical Chemists of
Serbia

in co-operation
with

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Boreskov Institute of Catalysis of Siberian Branch of the Russian Academy of Sciences

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MORPHOLOGY TRANSFORMATION INDUCED BY CALCINATION: FROM TITANIA NANOTUBES TO NANOPARTICLES

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ABSTRACT

Titanium dioxide nanotubes (TNT) synthesized via hydrothermal method and calcined at various temperatures, from 200-800 °C are characterized using X-ray diffraction (XRD), UV/Vis spectroscopy and scanning electron microscopy (FESEM). Tubular structure of as prepared TNT was most probably lost after calcination at 200 °C. Elongated forms of titania with different aspect ratios were observed after calcination at all temperatures lower than 800 °C. Calcination at 800 °C induced complete transformation of TNT to nanoparticles. Shape transformation was accompanied with changes in degree of crystallinity and different anatase to rutile crystal phase ratio.

INTRODUCTION

Nanocrystalline TiO_2 has attracted great interest in last few decades due to their unique properties, crystal structures, morphologies and promising applications in various fields, such as dye sensitized solar cells, photocatalysis, sensing and optoelectronic devices [1]. The TiO_2 is mainly used as photocatalytic material in the processes of water and air purification due to excellent photo and chemical stability, nontoxicity, superior redox ability and low cost [2]. The performances of TiO_2 nanomaterial are highly dependent on its crystal structure, size and shape [3]. Convenient hydrothermal synthetic route applied for synthesis of titania nanotubes (TNT), using highly basic dispersion of TiO_2 nanoparticles as a precursor, was the most commonly applied method in the last decade [4]. These nanotubes were further used as a precursor for synthesis of anisotropic (1D) TiO_2 nanocrystals of different crystalline structures capable of vectorial electron transport necessary for creating efficient photoconversion systems [5]. This paper is mainly devoted to characterization of elongated titania

nanoparticles obtained by calcination of hydrothermally synthesized TNTs, in the range of temperatures from 200 to 800 °C.

EXPERIMENTAL

Chemicals: TiO_2 powder (p.a., Fluka), NaOH (ZorkaPharm), HCl (conc. Aldrich) were used without further purification. Milli-Q deionized water was used as a solvent. Titania nanotubes were synthesized by a hydrothermal treatment (48 h/120 ^oC) of TiO_2 powder (Fluka) in proton deficient aqueous solution (10 mol/dm^3 NaOH) without shaking [3]. After autoclaving in Teflon vessel, the ensuing powder was separated from the solution using centrifuge. The powder was washed once using 1mol/dm^3 HCl aqueous solution for 2 h and then several times using pure water until the water reached pH = 7. Synthesized nanotubes were dried at 70 ^oC. Portions of TNT powder were calcined in an oven, at 200 - 800 ^0C. The sizes and shapes of the used titania nanoparticles were determined using FESEM TESCAN Mira3 XMU at 20kV instrument. XRD patterns of the TNT were obtained using standard powder diffraction methods with a Philips PW1830 X-ray powder diffractometer using Cu K_α line. UV/Vis spectroscopy was performed using Thermo Scientific Evolution 600 UV–Vis spectrophotometer.

RESULTS AND DISCUSSION

In Figure 1 XRD patterns of as prepared TNT and calcined TNT at different temperatures (TNT – 200 to 800) is presented. Peaks appearing in XRD patterns of as prepared TNT at 2θ = 25.4, 38, 48.3, 54, 55.2 and 62.9 deg., can be assigned as anatase TiO_2 crystal planes: 101, 004, 200, 105, 211 and 204, respectively (JCPDS No. 21-1272). The appearance of reflection at 2θ = 24.5 deg. suggests existence of monoclinic TiO_2 (*B*) structure (PDF 74-1940) usually described as built-up from corner- and edge-sharing octahedra, similarly to the anatase titanium dioxide. Also, this peak could be assigned to hydrogen titanate. Both compounds follow anatase structure of nanotubes synthesized using hydrothermal method. The development of the clear anatase crystalline phase with characteristic peaks

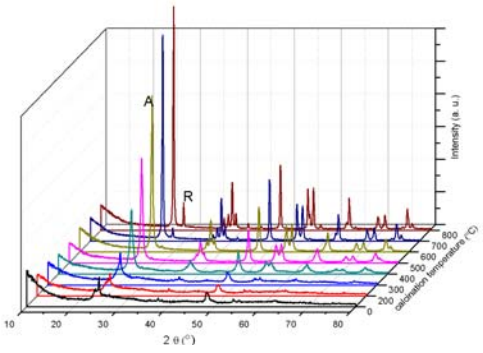

Figure 1 XRD patterns of as prepared and calcined TNT; calcination temperature presented as a z axis.

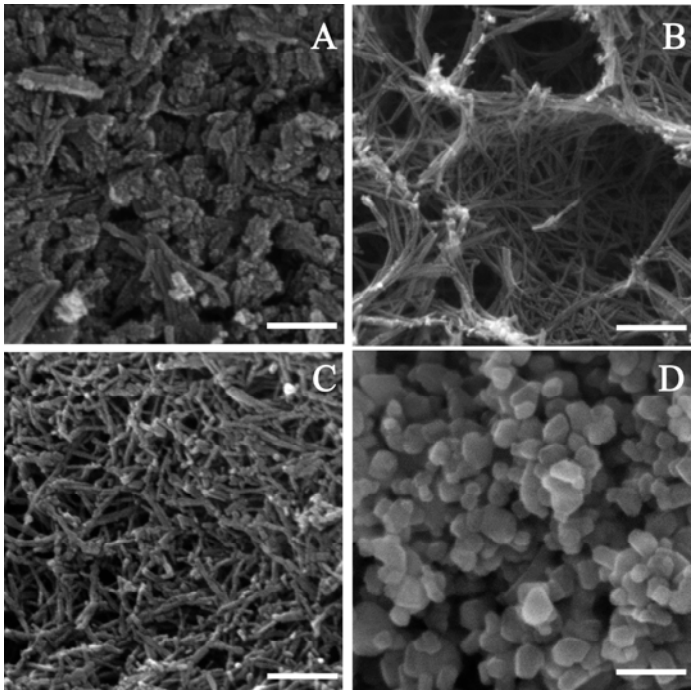

Figure 2 A typical FESEM images of as prepared (A) and calcined TNT samples at different temperatures: (B) 400 °C, (C) 600 °C, (D) 800 °C. Bar is 200 nm.

in XRD patterns at 2θ = 25.5, 37, 38, 39, 48, 54, 55, 62, 63, 69, 70, 74-76 deg. (JCPDS No. 21-1272) was observed for all calcined TNT samples. In the XRD pattern of the sample TNT-600, the appearance of the low intensity reflection at 2θ = 28 deg. suggested the initiation of the rutile phase formation. Calcination temperature increase to 700 °C induced further development of rutile crystalline phase which was confirmed by the increased intensity of the peak at 2θ = 28 deg. in the XRD pattern of the sample TNT - 700. In the sample calcined at 800 °C, the crystal phase composition consists of anatase and approximately 10 % of rutile. TEM measurements (not shown) confirmed expected morphology of as prepared TNT according to literature [5]. Reasonably uniform size distribution of tubes with outer diameter of about 10 nm and length that varies was observed. The changes in morphology of as prepared and calcined TNT were analyzed by FESEM, Fig. 2. Typical images of as prepared TNT, TNT- 400, TNT -600 and TNT -800 samples show that their morphology is significantly affected by the calcinations temperature. Until 400ºC no significant changes between as prepared (Fig. 2A) and calcined TNT can be seen except loss of tubular structure and formation of wire like structures. The FESEM image of TNT-400, Fig. 2B, reveals pretty much uniform cylindrical morphology of nanocrystals whose diameter is around 13 nm while the length varies until few hundred nanometers. In the morphology of

the sample TNT-600, Fig.2C, cylindrical shape predominate but the average outer diameter is slightly higher, 15 nm, while the length is little bit shorter in comparison to nanocrystals calcined at 400 °C. The morphology of the sample TNT-800 was completely changed in comparison to previously mentioned. Nanoparticles with almost bimodal size distribution of 71 and 91 nm were obtained, Figure 2D. Cylindrical morphology in this sample completely disappeared and also the particles agglomeration increased, according to FESEM image. Despite significant changes in morphology between as prepared and calcined TNT, almost no changes in UV/Vis reflection spectra can be observed. All samples had absorption threshold at about 3.2 eV.

CONCLUSION

Titania nanotubes were successfully synthesized using hydrothermal method. They were used for preparation of different elongated titania nanocrystals by calcination in air. Obtained samples had different shapes, sizes and degree of crystallinity as well as different ratio between anatase/rutile crystalline phases. Anatase phase is dominant in all samples, even ones calcined at higher temperatures (700 – 800 °C), while the rutile phase formation was substantially postponed. Results showed that by increasing calcination temperature the degree of crystallinity also increases while the aspect ratio of titania nanoparticles decreases until almost spherical particles are obtained after calcination at 800°C.

ACKNOWLEDGEMENT

This work was partially supported by the Ministry for Science of the Republic of Serbia (Grants no. 172056 and 45020).

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