

# Synthesis of High Surface Area Titania Based Nanoparticles and the Effect of Surfactants

Alp Yurum<sup>1</sup>, Miad Yarali<sup>2</sup>, Selmiye Alkan Gürsel<sup>2</sup>

<sup>1</sup> Sabanci University Nanotechnology Research and Application Center, Tuzla, Istanbul 34956, Turkey

<sup>2</sup> Faculty of Engineering and Natural Sciences, Sabanci University, Tuzla, Istanbul 34956, Turkey

ayurum@sabanciuniv.edu

## Abstract

In this study, TiO<sub>2</sub> based nanotubes and nanosheets were synthesized to be used as an adsorbent and support in various processes. As a starting material, sol-gel synthesized anatase and commercial anatase were used. TiO<sub>2</sub> was converted to high surface area hydrogen titanate (H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>) and sodium titanate (Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>) nanotubes and nanosheets under alkaline conditions with hydrothermal treatment. In addition, synthesized materials were modified with surfactants (dodecyl amine, cetyl trimethylammonium bromide) to enhance the surface properties. XRD, TGA, SEM, and BET analyses were utilized to characterize the materials. The results suggest that synthesized materials with their high surface areas and active surfaces are promising materials for energy and water treatment areas.

## Introduction

The nanostructured TiO<sub>2</sub> materials other than anatase structure having layered structure are alkali titanates (A<sub>2</sub>Ti<sub>n</sub>O<sub>2n+1</sub>), protonic titanate (H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>), and lepidocrotic species. The unique mesoporous, high surface area properties of these materials offer promising results as semiconductors, catalytic materials and adsorbents [1]. The synthesis of alkali titanates with wet methods is possible with both a solid-state reaction by treating TiO<sub>2</sub> with alkali carbonate-peroxide mixtures [2] and hydrothermal treatment with strong basic solutions [3].

In the present study, synthesis of mesoporous titanate species, which were produced from commercial anatase (COM), and synthetic TiO<sub>2</sub> produced by sol-gel technique (SG) were studied. The effect of hydrothermal synthesis conditions on the structure was also examined.

## Experimental

For the synthesis of SG, titanium tetraisopropoxide was used as a precursor. After obtaining the gel, samples were calcined at various temperatures to optimize the surface properties. After that step, SG and COM were treated with 10 M NaOH solutions at various temperatures and durations to see the effect experimental parameters on the structure of titanates. Finally, after hydrothermal treatment, samples were washed with either DI water or HCl solution to obtain Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> or H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> respectively. As an additional step, surfactants were added before starting the hydrothermal treatment. At every step, the structural characterization of the samples were done using SEM, TGA, XRD, and BET techniques.

## Results & Discussions

XRD characterization of COM and SG revealed that both of the samples are pure anatase. However, it can clearly be seen that the crystallinity is higher for COM sample when compared with SG version. The peaks show that SG samples have smaller crystallite size. The XRD patterns also show that with increasing calcination temperatures, crystallite sizes start to increase.

SEM images reveal that while the size of SG particles is about 10 nm, the size of COM particles is around 200 nm. After hydrothermal treatment, both the morphology and crystal structure of the samples changed. After 24 hours of treatment, titanate structures started to appear but XRD patterns show that there is still anatase phase available in the structure. However, after 48 hours of treatment, the samples are completely of titanate structure (Figure 1). Interestingly, SG and COM yielded different morphologies. While COM samples after 24 hours of hydrothermal treatment transformed to nanotubes, SG samples transformed to nanosheets. At the end of 48 hour of treatment, the SG particles finally transformed to nanotubes. The nanotubes obtained have a diameter of 30 nm and similarly the thickness of the plates is about 30 nm (Figure 2). After the hydrothermal treatment, washing the sample with HCl solution had a significant effect on the crystal structure. The peak around 10° corresponds to (200) and it is related to the distance between the titanate layers. With acid washing, the layers expanded. Also synthesizing titanates in the presence of surfactants affected the structure of particles. While nanotubes were obtained, these nanotubes had a diameter of 40 nm. These nanotubes entangled to each other forming sheets and these sheets were stacked on each other.

The specific surface areas of SG and COM are 66 and 40 m<sup>2</sup>/g respectively. After hydrothermal treatment, the surfaces areas obtained ranges from 141 to 169 m<sup>2</sup>/g. This increase in surface area is due to the layered structure of titanates. Pore size distribution (PSD) curve of the sample treated for 48 hours reveal a very sharp peak at 9.9 Å (Figure 3). This is the interlayer distance of titanates obtained. This distance increases with acid washing. Addition of the surfactants increases this distance further to 12.5 Å. Thanks to this expansion, atoms can easily enter and leave the structure. By exfoliating the titanate layers, more surfaces can be exposed and these materials can be used in areas like energy and water treatment.

## Conclusion

Nanostructured mesoporous titanate samples were synthesized with hydrothermal treatment under alkaline conditions from commercial and sol-gel synthesized anatase. Both the commercial and sol-gel derivative with their mesoporous structure possess high surface areas with expanded layers. As a future study the exfoliated titanates will be used either as a support material or adsorbent for water remediation processes.

## References

- [1] B. K. Erdural, A. Yurum, U. Bakir, G. Karakas, J. Nanosci. Nanotechnol., **8** (2008) 878.
- [2] M. Watanabe, J. Solid State Chem., **36** (1981) 91.
- [3] M. Tomiha, N. Masaki, S. Uchida, T. Sato, J. Mater. Sci., **37** (2002) 2341.

## Figures

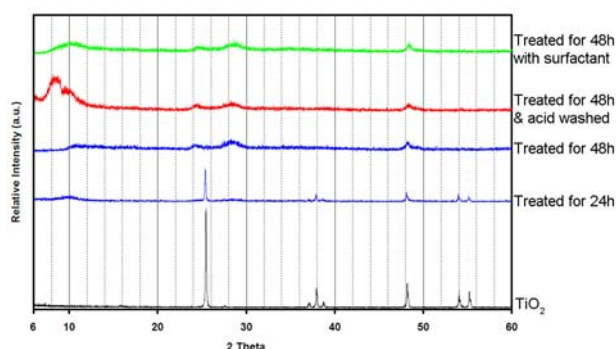


Figure 1. XRD patterns of hydrothermally treated commercial anatase

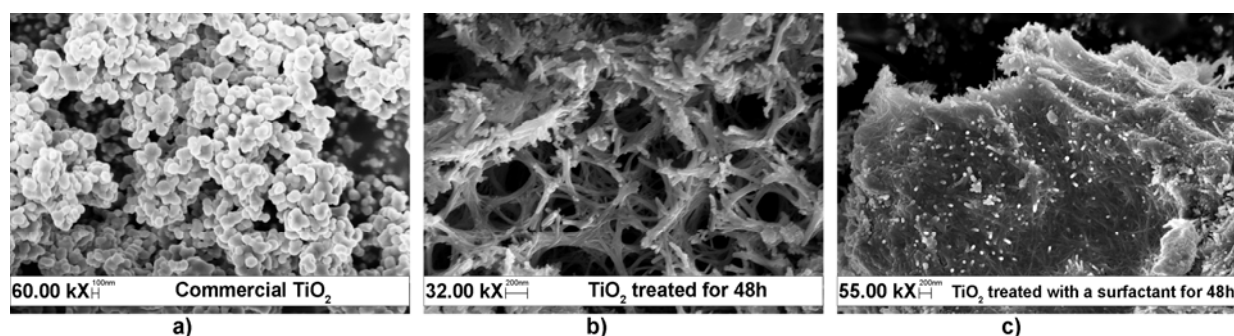


Figure 2. SEM images of hydrothermally treated commercial anatase

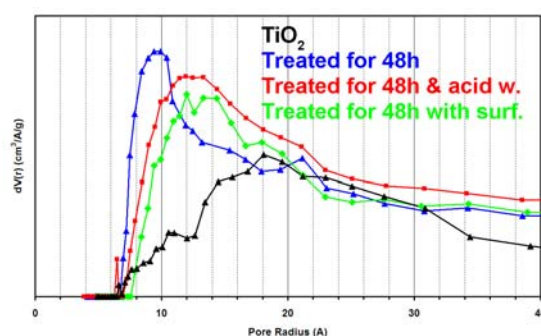


Figure 3. Pore size distribution curves of hydrothermally treated commercial anatase