doi:10.1017/S1431927611009378
Microsc. Microanal. 17 (Suppl 2), 2011


# Transmission Electron Microscopy Study of $TiO_2$ Anatase Crystal Morphology Prepared by Hydrothermal Synthesis

B. Horvat, G. Drazic

Department for Nanostructured Materials, Jozef Stefan Institute, Ljubljana1000, Slovenia

Nanocrystalline $TiO_2$ is one of the most studied oxides due to its extensive use in photocatalysis, solar energy conversion, sensors, mesoporous membranes, food, cosmetics, pigments, etc. Its properties can be controlled by its particle size, morphology and crystalline form (anatase, rutile or brookite) [1]. When $TiO_2$ is prepared by hydrothermal synthesis from Ti (IV) isopropoxide in water or ethanol, the product is always in anatase form with small amount of brookite in slightly acidic growth conditions [2].

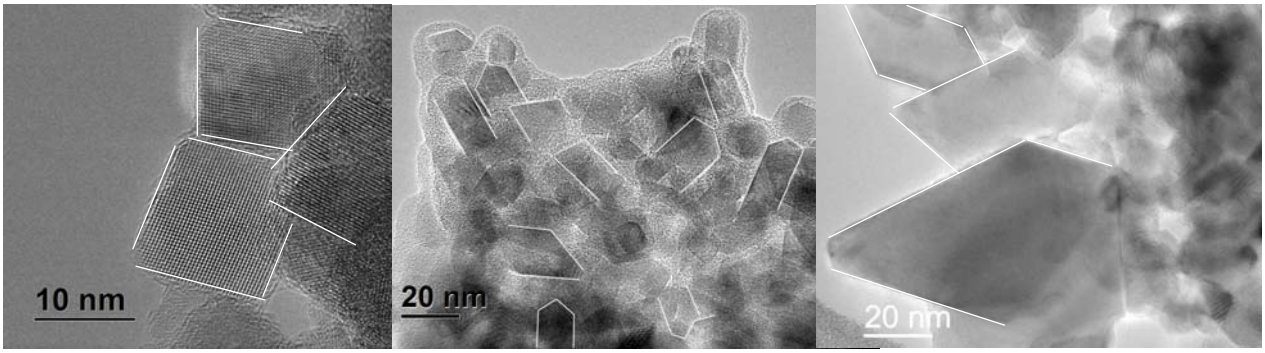
In the literature the crystal growth of $TiO_2$ during hydrothermal synthesis was studied extensively. Cho et.al. [3] suggested growth model of bipyramidal anatase crystals, using $TiCl_4$ as source of Ti, in alkaline conditions at temperatures above 200°C where in the first stage formation and growth of anatase nuclei takes place. Second step is rapid growth along [001] direction by oriented attachments between (001) faces to produce an elongated structure with zigzag {101} faces. In third stage zigzag {101} pyramidal faces flatten by solution and precipitation mechanism and in final growth stage rapid growth with Ostwald ripening along [001] direction take place. They observed that the longer the time and the higher the temperature of hydrothermal synthesis, the more defined and bigger bipyramidal crystals appear. Deng et.al. [4] described growth of large anatase monocrystal bipyramids in range of few microns produced with hydrothermal synthesis at 200 °C for 48 h from pH 5.6 to pH 11 starting from titanate nanowires which dissolve under alkaline conditions, anatase nuclei are formed, from which with Ostwald ripening truncated octahedral bipyramids seeds appeared. Using the addition of various ions (like fluorine anions) different morphologies, like plates and/or truncated bipyramides could be prepared with exposed diverse terminal planes which have different photocatalytic efficiency [5]. There is not much data in the literature for low-temperature hydrothermal synthesis of $TiO_2$ anatase particles, which could be important for applications where temperature above 100°C should be avoided.

The aim of the present work was to study the nucleation and crystallization of anatase particles prepared by hydrothermal synthesis at lower temperatures. No surface active compounds or pH controlling substances were added to the system. To achieve the equilibrium long times (typically in the order of 100 hours) were used. Experiments were done consecutively, after 100 hours at 20°C the system was heated up for 10°C for next 100 hours and so on for the temperatures up to 100°C. After this series of experiment temperatures 150 and 200 °C were also used. The size, morphology and crystallization degree were studied using Jeol 2010 and Jeol 2010 FEG transmission electron microscopes, equipped with GATAN slow-CCD cameras.

In Fig. 1 the TEM micrographs of $TiO_2$ anatase particles prepared at temperatures 40, 80 and 200°C are displayed. In first case particles are mostly in the form of prisms (oblique rectangular) with {101} exposed planes. After 100 hours at 80 °C prisms became elongated and characteristic pyramidal angles star to appear. At 200 °C larger (up to 100 nm) bipyramides are formed. The morphology of the anatase crystals influences the photocatalytic efficiency [6].

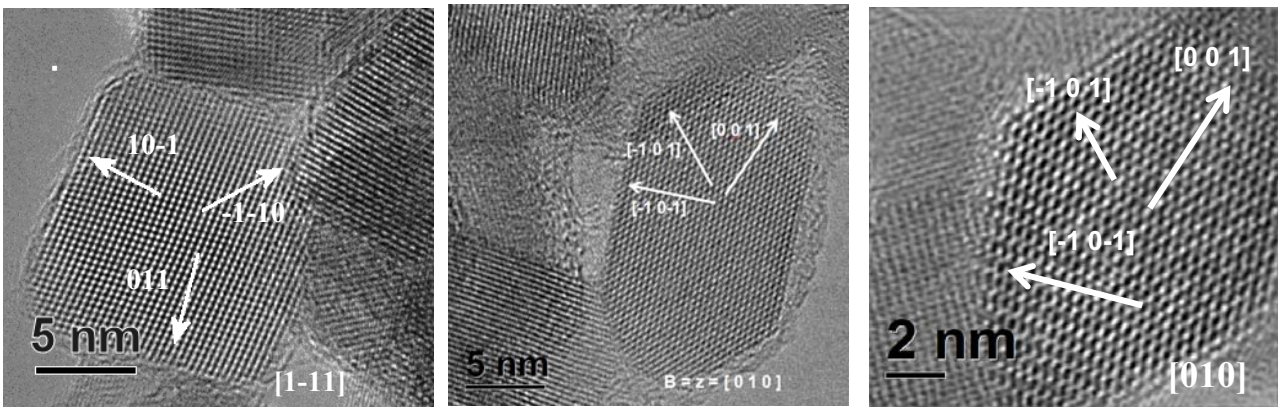
References

[1] A. L. Linsebigler et al., *Chem. Rev.*, 95, (1995), 735
[2] A. Di Paola et al., *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 317, (2008), 366
[3] C. H. Cho et al., *Materials Chemistry and Physics*, 92, (2005), 104
[4] Q. Deng et al., *Journal of Crystal Growth,* 312, (2010), 213
[5] J. Pan et al., *Angew. Chem. Int. Ed.* 50, (2011), 1
[6] This work is part of the PhD thesis of Ms. Barbara Horvat and was financially supported by the Slovenian Research Agency under Grant No. 1000-08-310086




100h at 40°C 100h at 80 °C 150h at 200 °C

FIG. 1. TEM images of the particles prepared by hydrothermal synthesis at different temperatures.




100h at 40°C 100h at 80 °C 100h at 200 °C

FIG. 2. HRTEM micrographs of individual morphologies prepared at different temperatures.

https://doi.org/10.1017/S1431927611009378 Published online by Cambridge University Press