Preliminary Report: Mechanistic studies of titania synthesis and rutile-anatase phase transition in the course of the reaction in non-aqueous medium

Proposal summary:

The overall goal of this project was to develop a crystallization strategy to predict and control the occurrence of polymorphs in a non-aqueous system. The emerging question was the mechanism of the observed crystal phase and shape transition of titanium dioxide nanoparticles. The process of most interest was the reversible transition of the rutile-to-anatase during the course of chemical reaction. The challenge was to be able to collect the complementary information about the structure, short- and long-range order, and the size of nanoparticles. Applying the in-situ Raman-X-ray diffraction/absorption techniques provided an opportunity to study the complete reactions, nucleation, crystallization, growth, and most importantly the phase transition.

Experimental method

The experiment was performed at the Swiss-Norwegian beamline. For in-situ studies a new spectroscopic cell was successfully used (Figure 1). Prof. Sankar Gopinathan, University College London, UK, designed the cell. It allows X-ray absorption measurements in transmission and fluorescence modes. We tested the cell at varying operating conditions with windows made out of mica, mylar and kapton. For testing of in-situ cell in: (a) fluorescence mode we used titania nanoparticles synthesis and (b) in transmission mode we used copper nanoparticles synthesis.

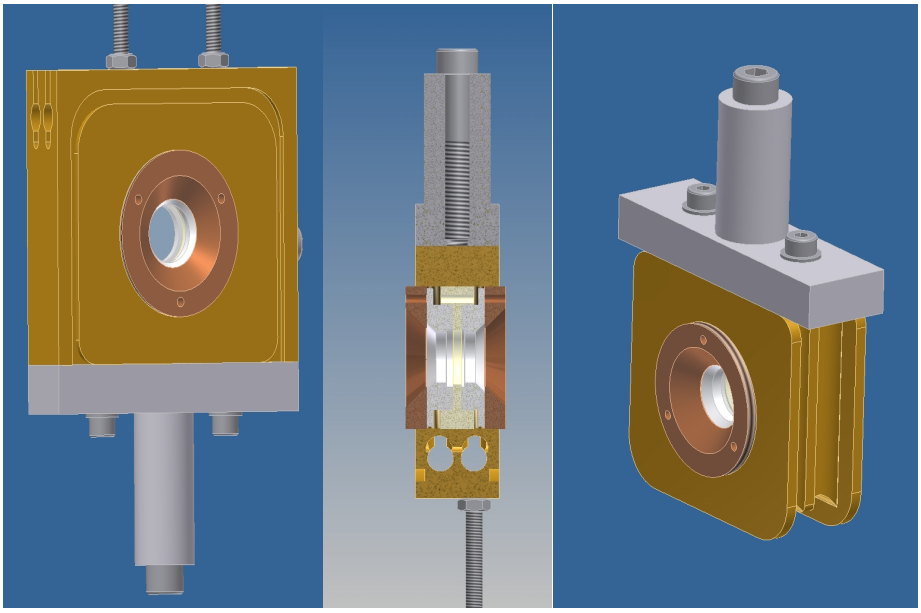

Figure 1 The schematic drawing of the in-situ cell: (left) the cell assembled inside the heating frame. The heating frame has U-shape and incorporates 4 heating cartridges; (middle) the cross-section of the cell showing the dimension inside the cell; (right) the cell, isolated from the heating frame.

XRD, XAS and simultaneous Raman measurements were performed at temperature range between RT and 180°C. Explaining of the mechanism of phase transition on nanoscale requires knowledge of the structure and composition of the nanoparticles as they react. Experiments at the Ti K alpha edge were possible with the Vortex fluorescence detector available at SNBL. The green laser, used for Raman studies, ensured that we are gaining information on organic counterpart of the inorganic nanoparticle synthesis. This was crucial for the phase transitions. We investigated the reactions of titanium tetrachloride in acetone and benzyl alcohol.

Results:

Despite several reports of non-aqueous synthesis and crystallization mechanism of anatase nanoparticles, [1-6] no strategy to either change or control crystal phase during the course of the reaction has been proposed.

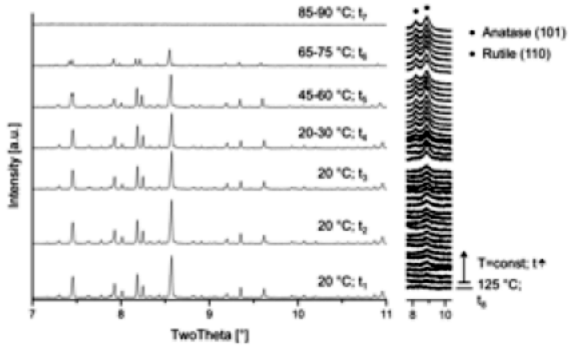

Figure 2 X-ray diffraction patterns taken in-situ during the course of titania nanoparticles synthesis. (left) diffraction pattern taken at different temperatures between 20 and 90°C. (right) Spectra taken at 125°C at different time of reaction between 0 and 41 hours.

In our recent ex-situ studies we observe the rutile-anatase phase transition of two different systems; thus we believe that our observation seems to be generally valid for non-aqueous systems. Figure 1 shows our in-situ studies of titania synthesis in acetone at SNBL. These in-situ XRD measurements give a direct proof of our ex-situ observation: first the thermodynamically stable rutile phase is formed (1-24 hours) and only than anatase is formed (41 hours). This is an exciting result since up to now this transition was believed to be thermodynamically unfavorable and was never experimentally observed.[6]
A completely surprising is crystallinity of the starting reaction mixture. Obviously if titanium tetrachloride is mixed with acetone at RT, an unknown crystalline intermediate phase is formed. We are currently investigating the crystal structure and the exact composition of this phase (see also Figure 3 left). When the cell is heated above 90°C this unknown crystal phase completely disappears. X-ray absorption spectroscopy bridges the gap in XRD measurements between the dissolution of the intermediate phase and crystallization of rutile nanoparticles.
An example of XANES is given in Figure 3. We observed very pronounce changes in the pre-edge features transitions even though no crystalline nanoparticles are observed in XRD studies (Figure 3 left). In the time range between 6-41 hours where the crystal phase transition takes place we observe corresponding pre-edge and edge features changes. However, the spectra features of reference anatase and rutile nanopowders (not

show here) and nanoparticles in solution strongly differ. The principal components analysis is in progress.
Furthermore we collected EXAFS spectra during the course of reaction and EXAFS of reference powder spectra of anatase and rutile nanoparticles (not shown here). These should shade the light on the coordination of Ti and distances of Ti-O, Ti-Cl and Ti-Ti. Data analysis is under progress.

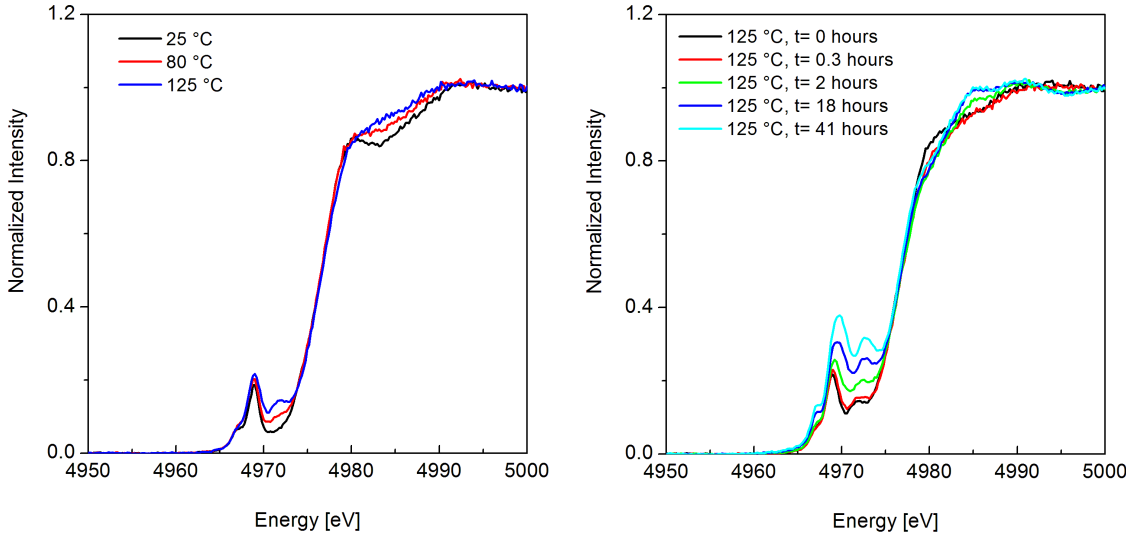

Figure 3 In-situ evaluation of the Ti K alpha edge XANES signal during the course of titania nanoparticles synthesis. (left) Spectra taken at different temperatures steps: 25, 80 and 125°C. (right) Spectra taken at 125°C at different time of reaction between 0 and 41 hours.

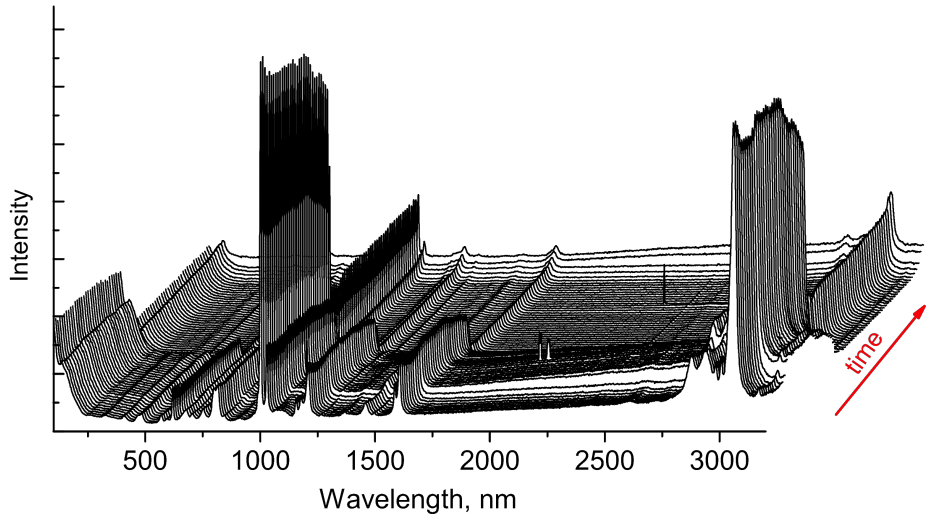

Figure 4 Raman spectra of titania nanoparticles synthesis in benzyl alcohol recorded in-situ during the course of the reaction. Time span is from 0 to 80 minutes.

In order to learn more about the changes of organic phase during the inorganic synthesis we measure Raman up to 3100 nm. From previous studies we know that reaction medium

plays crucial role in inorganic synthesis. An example is given in Figure 4 where we clearly see the evolution of bands corresponding to benzyl alcohol and titania. The work on determining the spectators from active species in reaction is in progress.

The study demonstrate that:

- important structural information on crystallization and phase transitions can be only gained in the in-situ conditions using complementary Raman-X-ray diffraction/absorption techniques.
- A number of studies have assumed that the rutile-to-anatase transition is thermodynamically not possible. However, we experimentally proofed that it is indeed possible. Furthermore, we are presently working on mechanism of this transition.

Note: This is a preliminary report, which will be replaced by a comprehensive report in the future. Data evaluation, improvement of the cell heating performance and manuscript preparations are under progress.

References

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