

## Analysis of Fluorine Traces in TiO<sub>2</sub> Nanoplatelets by SEM/EDX, AES and TOF-SIMS

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The synthesis of TiO<sub>2</sub> nanoplatelets (see Fig. 1 top left) with fluorine-containing reactants is carried out using titanium (IV) butoxide as precursor and concentrated HF as shape controller [1]. The final product requires a working up in order to eliminate or at least to reduce the amount of residual fluorides, which is realized here by well-defined thermal treatment of the samples. Bulk and surface sensitive methods namely scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), Auger electron spectroscopy (AES) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) have been applied to trace the presence of any fluorides in dependence on different information depths and measurement sensitivities of these analytical methods.

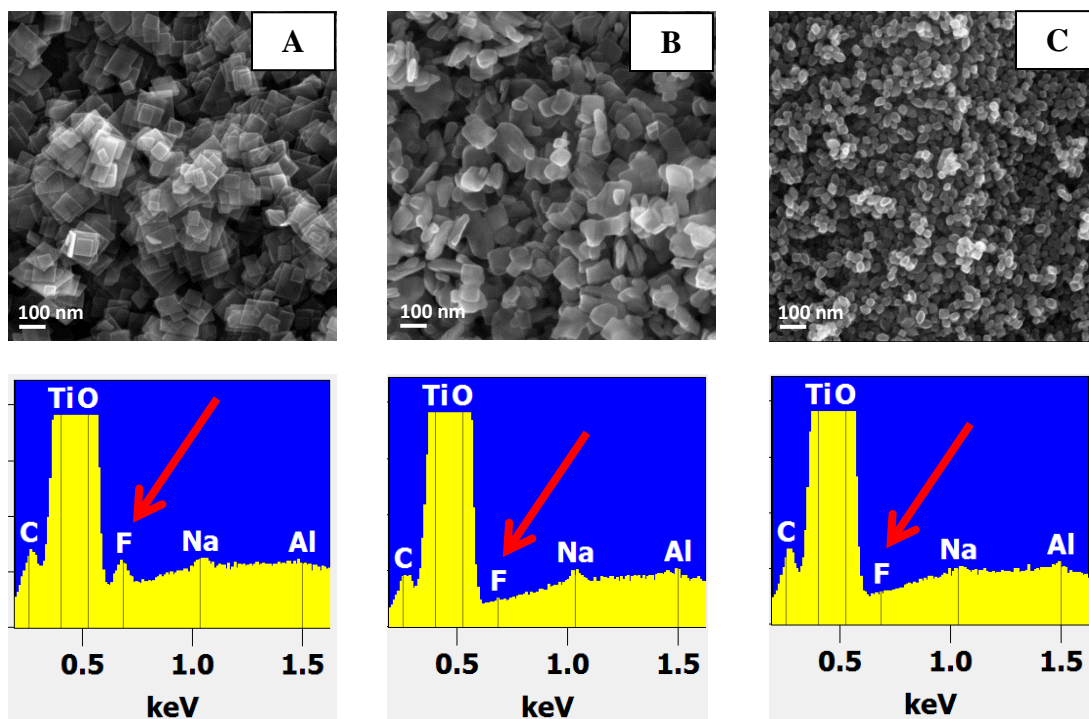
Qualitative investigation of the bulk elemental composition of TiO<sub>2</sub> nanoplatelets by means of EDX has identified - as expected - fluorine in case of the as-synthesized samples (Fig. 1 bottom left). In contrast to this, EDX spectra of thermally treated products exhibit either fluorine content in the range of the limit of detection (Fig. 1 bottom middle). This holds also true for the reference, fluorine-free sample, TiO<sub>2</sub> nanoparticles of bipyramidal shape (Fig. 1 bottom right) [2-5]. This type of material has been prepared by a different synthesis route. Corresponding SEM images of calcinated and reference sample are shown in Fig. 1 top middle and right, respectively. From the SEM micrographs the as-prepared nanoplatelets with sharp/defined edges are clearly visible. In contrast to this appearance of the platelets, the thermally treated sample shows platelets, too, but their morphology differs; they have a more irregular shape and the edges are not sharp anymore (they look as if they are „melted together“). Obviously, the heating had an influence on their shape.

For distinction whether fluorine is present only at the surface of the TiO<sub>2</sub> nanoplatelets, top-surface sensitive AES and ToF-SIMS spectra have been collected and analyzed. As a result, secondary ions of fluorine are detected in ToF-SIMS spectra of all samples, but could be roughly quantified by measurement of the same reference sample as for EDX, namely TiO<sub>2</sub> nano-bipyramids. This revealed that the amount of fluorine up to one nanometer depth beneath the surface is reduced in the thermally treated specimen compared to the raw product down to a concentration about as low as in the reference sample. In contrast to the ensemble (analyzed area at the surface) method ToF-SIMS, AES as a surface sensitive method, too, allows analyzing elemental and, sometimes, chemical state of the first few nanometers from the top-surface of individual NPs by point analysis with a lateral resolution below the nanoplatelets size [6]. First AES measurements have been undertaken and a F KLL peak has been clearly detected at the surface of samples of as-prepared TiO<sub>2</sub> nanoplatelets under optimized measurement conditions. F KLL was not detectable after sample calcination, which is in agreement with ToF-SIMS results. Moreover, high resolution AES measurement of single TiO<sub>2</sub> nanoplatelets elucidated that the surface atomic layers surrounding the TiO<sub>2</sub> nanoparticles contain fluorides before the thermal treatment of the NPs.

Further AES measurements of calcinated single NPs are currently performed to be added to the whole picture and possibly relate the results to structural effects such as e. g. growth of coherent X-ray scattering domains by annealing TiO<sub>2</sub> nanoplatelets.

#### References:

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**Figure 1.** SEM micrographs (top row) and corresponding EDX spectra (middle row) of A) as-prepared TiO<sub>2</sub> nanoplatelets B) annealed TiO<sub>2</sub> nanoplatelets, and C) reference TiO<sub>2</sub> nanoparticles of biipyramidal shape; red arrows show the F K $\alpha$  peak in EDX spectra.