Structural properties of sol-gel synthesized Li^+-doped titania nanowhisker arrays

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Nanostructured titania is of particular interest for applications in photo-catalysis due to its high catalytic activity. Moreover, these structures are of particular interest for many applications due to their electronic properties, e.g. anti-reflection layers, sensors, vacuum microelectronics. The band gap of the nanoscaled semiconducting anatase is size dependent. The band gap increases in the size range of 15 nm to 3.9 eV [1], compared to the bulk value of 3.2 eV [2], suggesting already a quantum confinement effect. Nanowhiskers, grown in even smaller dimensions as in this study are prospective candidates for showing a transition to the quantum confinement effect.

Sol-gel synthesis of mesoporous oxides relies on the self-assembly of the structure directing agents, the surfactants which rule the solidification or crystallisation of the inorganic oxide. Mesoporous ordered solids produced by sol-gel processing are e.g. monolithic SBA-15 type silica networks or the highly catalytically active mesoporous titania powders. In this study titania nanowhisker arrays with a high surface area were produced.

Anatase nanowhiskers were grown in a sol-gel process [3] using ethylene glycol modified titanium(IV) (EGMT) as the titania precursor and Lithiumdodecyl sulphate (LDS) as a structure directing agent. The LDS simultaneously delivers the Li^+ as a dopant. After synthesis the samples were dried and calcined in order to remove the surfactant. The samples were characterised by X-ray powder-diffractometry.

The dried samples were found to consist of an approximately proportionate equal mixture of rutile and anatase. The high temperature phase of titania grows thus even under room temperature processing. After calcination at 400 °C for 4 h, the intensity of the anatase peak grew significantly, indicating a higher anatase ratio. After calcination nitrogen sorption measurements were performed in order to determine the average pore sizes as well as the specific surface areas.

The resulting samples were investigated by HRTEM. The samples showed a strong growth anisotropy, i.e. the whiskers revealed a high aspect ratio. The diameter of the whiskers measures approximately 3 – 4 nm and the length up to 50 nm even after calcination. The titania crystals grew as whiskers with a preferential orientation. These needles are aggregated to radial bunches, thus forming nanowhisker arrays.

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Calcination caused the formation of roundish nanoparticles on top of the whisker tips. These crystalline particles are associated with an amorphous phase and were attributed to the anatase phase.

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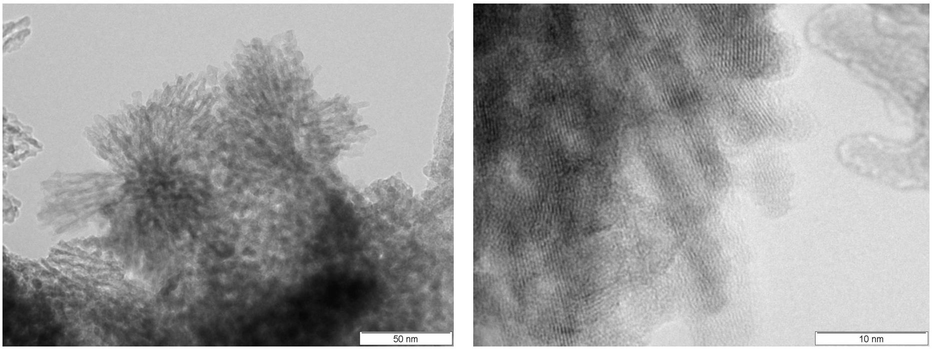

Figure 1. Left: Survey of nanowhisker arrays in the sample after calcination for 4 h at 400 °C. Right: HRTEM micrograph showing the whiskers with some roundish particles.

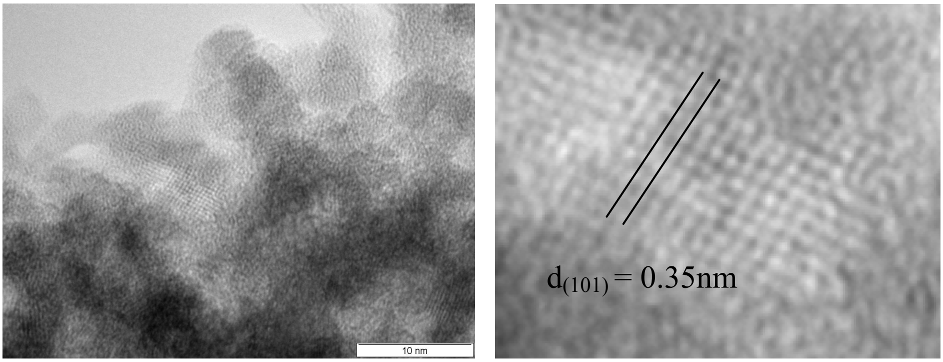

Figure 2. Left: Roundish particles observed after calcination for 4 h at 400 °C. Right: HRTEM micrograph. Detail of one particle of Fig. 2 left, identified as anatase with 0.35 nm d-spacing of the (101) plane.