Titanyl sulfate as template for preparation of 1D titania structures

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One-dimensional (1D) nanostructured inorganic materials (nanowires, nanorods, or nanotubes) are interesting from various aspects. Such structures can be considered as building blocks for sensors, electronics, photonics, and bioelectronics applications. Their potential relies on the subtle control of their physical properties, which are based on their atomic scale structures, and their 1D morphology, i.e., their length and diameter dimensions at the nano- and microscale. By controlling these parameters, a variety of chemical and physical properties can be tailored [1,2].

Titanyl sulfate can serve as a template for preparation of 1D titania structures. When immersed in aqueous ammonia at a temperature of about 0 °C the crystals of titanyl sulfate provide solid residue composed of particles, whose shape and dimensions correspond perfectly to the particle morphology of the initial titanyl sulfate with composition matching that of metatitanic acid. On annealing, the material transforms above 400 °C to anatase and subsequently above ~1100 °C to rutile while perfectly maintaining the size and shape of the original particles. Particle shape of the two starting materials (TSD and TSM) is distinctly different (Figure 1). Sample TSD consists of regular rod-like crystals with the size of about 10−15 × 2 μm, whereas sample TSM is formed by aggregates of isometric crystals with broad size distribution. XRD patterns show that sample TSM corresponds to titanyl sulfate monohydrate ($TiOSO_4 \cdot H_2O$) with a known structure while sample TSD consists of titanyl sulfate dihydrate ($TiOSO_4 \cdot 2H_2O$) of which the structure has not been determined yet [3]. As a part of this study, we solved the structure of titanyl sulfate dihydrate using dynamical refinement of precession electron diffraction tomography data [4].

The particle shape of TSD and TSM samples is determined by the atomic structure of the corresponding TS (Figure 1). The rod-like shape of TSD sample is the result of 1D morphology of $(TiO_5)_n$ helices mutually bound only by weak H-bonds in the structure of TSD. On the contrary, TSM forms a 3D framework connected through Ti−O and S−O bonds, while H_2O molecules only fill the small channels in the structure. TSM sample therefore occurs as isometric crystals. In both structures, the chains or helices formed by TiO_6 corner-sharing octahedra are spaced with sulfate ions and water molecules. During the reaction with ammonia leaching of sulfate anions and their replacement with OH^- anions take place.. When the structure loses the sulfate ions holding the $(TiO_6)_n$ chains/helices in shape, the helices of corner sharing octahedra most likely stretch out a little bit when repelled by H−H interaction resulting in polymer-like chains of TiO_6 octahedra similar for both samples, and characteristic of the amorphous metatitanic acid.

It has been shown that the metatitanic pseudomorphs after TSD have excellent sorption properties for radioactive isotopes. Since the size and morphology of the hydrated titanyl sulfate particles can be varied within wide limits by the conditions of its crystallization [3], the described method opens a new pathway to obtain particles of various titanium oxide compounds of desired shape and size.

References:
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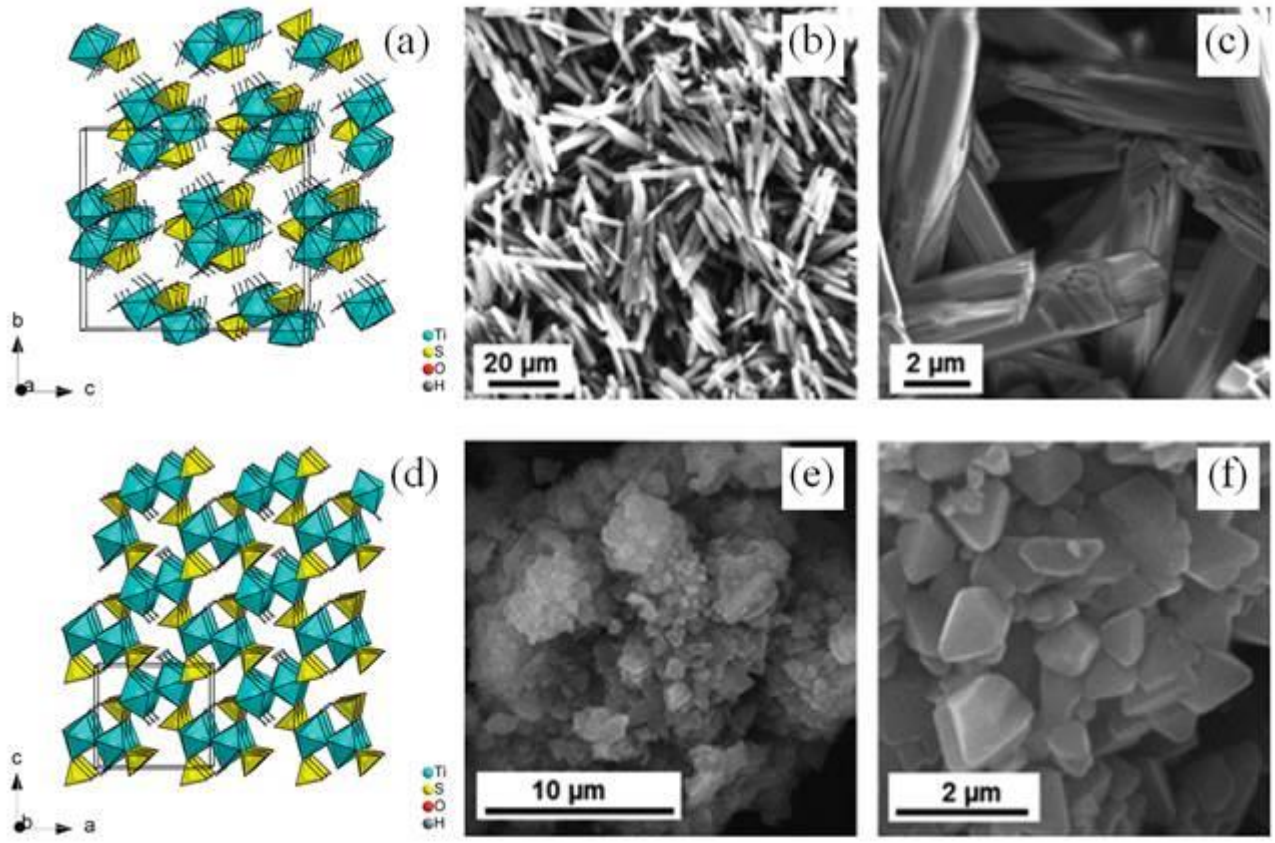

Figure 1. Structure of titanyl sulfate dihydrate (a) and titanyl sulfate monohydrate (d), and the corresponding metatitanic acid pseudomorphs (after titanyl sulfate dihydrate - b,c, and after titanyl sulfate monohydrate - e,f).