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Metatitanic acid pseudomorphs after titanyl sulfates: nanostructured sorbents and precursors for crystalline titania with desired particle size and shape

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KEYWORDS: metatitanic acid, titania, pseudomorph, titanyl sulfate dihydrate structure, morphology control, sorption, radionuclides

ABSTRACT: A new preparation method for the synthesis of TiO_2 microrods in aqueous media starting with solid hydrated titanyl sulfate crystals with defined morphology is presented. The method is based on the extraction of sulfate ions from the crystals and their replacement with hydroxyl groups in aqueous ammonia solution leaving the Ti-O framework intact. The particle size and morphology of the starting hydrated titanyl sulfate is closely preserved in the pseudomorphs of amorphous metatitanic acid including such details like the layered structure of the original hydrated titanyl sulfate crystals. When annealed up to 1200 °C, the rod-like morphology of particles is retained, while the phase composition changes to anatase/rutile. The rod-like particles of metatitanic acid possess excellent sorption properties towards radionuclides. The mechanism of pseudomorph formation is discussed based on the structures of the precursors, including the hitherto unknown structure of titanyl sulfate dihydrate determined by electron diffraction tomography.

INTRODUCTION

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 nano- and microscale. By controlling these parameters, variety of chemical and physical properties can be tailored[1-2]. For example, it has been demonstrated that morphology and textural parameters such as particle shape, size, surface area, porosity, and dimension (1-, 2-, 3-D) affect the light absorption capability of catalysts[3]. By engineering the dimensions and morphology of a material, the incident light can be scattered on the surface, which can lead to reabsorption of the scattered light, and thus the number of photons that penetrate into the catalyst will increase[4].

Titania (TiO_2), one of the most studied catalyst nowadays[5-9], has been extensively investigated in a variety of fields due to its stability, high electron mobility, and wide band gap between the valence and conduction bands. It has been used as an electrode in dye-sensitized photovoltaic cells[10-13], and as a water-splitting catalyst for hydrogen generation[14]. In these applications, the morphological parameters of titania significantly influence the performance of the respective devices[15]. It has been shown that particle size and shape, crystallinity, surface morphology and chemistry of the TiO_2 material are the key parameters to be controlled for optimized performance of the solar cell[13].

Recently, TiO_2 nanotubes[16] have attracted a great deal of interest because of their large surface area, ion-changeable ability, photocatalytic ability for catalysis applications[17-19], gas sensing[19], dye-sensitized solar cells[18-19], and photovoltaics[20]. Previously proposed methods for the preparation of tube-like TiO_2 include assisted template method[21-22], electrochemical anodic oxidation[16], sol-gel process[23], and hydrothermal treatment[24-25]. However, most of these methods are high-temperature processes that require expensive preparation instruments or precursors. TiO_2 nanotubes produced by using these methods commonly have tube diameters that range from approximately 70 to 100 nm.

Lately, titania aggregates in form of rods or tubes morphologically related to typical forms of titanyl sulfate were described[10]. Both the rods and tubes described in this article consist of nanocrystalline anatase particles. However, authors of this publication ascribed formation of this shape to action of surfactant added (CTAB).

In this work, we describe the transformation of titanyl sulfate monohydrate and titanyl sulfate dihydrate in aqueous medium under specific reaction conditions to the reaction product, hydrated titanium dioxide, which perfectly preserves the shape and dimensions of the micrometer-size particles of the starting material. Possible mechanism of transformation is discussed based on the structural and morphological relationships between the starting titanyl sulfate and the products. Characterization of the product shows that the resulting pseudomorphs correspond to the substance described in the literature as metatitanic acid. Since the size and morphology of the hydrated titanyl sulfate particles can be varied within wide limits by the conditions of its crystallization[26], the described method opens a new pathway to obtain particles of various titanium oxide compounds of desired shape and size. It has also been shown that the material has excellent sorption properties for radioactive isotopes.

EXPERIMENTAL SECTION

Chemicals

Two types of titanium(IV) oxysulfate ($TiOSO_4 \cdot nH_2O$ - commonly referred to as titanyl sulfate - TS) were used as starting material for synthesis. Both titanyl sulfates were checked by powder XRD, and it was found out that the two materials are structurally very different (Figure S1). The commercial titanyl sulfate supplied by Sigma Aldrich (min. 29 % Ti as TiO_2 basis, technical grade purity) corresponds to titanyl sulfate dihydrate ($TiOSO_4.2H_2O$), and it is labelled TSD hereafter. Another titanyl sulfate obtained from the Czech producer of titanium dioxide pigments Precheza (Přerov, Czech Republic) corresponds to titanyl sulfate monohydrate ($TiOSO_4.H_2O$), and it is labeled TSM. Aqueous solution of ammonia (analytical grade purity, 25-29 %, Penta, Czech Republic) was used in the synthesis.

Synthesis

100 mL of cooled distilled water was mixed with 50 g of ice, and 5 mL of aqueous ammonia. After adding 4.80 g of titanyl sulfate, the suspension had temperature of 0 °C and pH 9. While the mixture was magnetically stirred for 4 hours at pH 9, its temperature rose to 24 °C (room temperature – RT). Then the suspension was decanted twice, the solid residue was filtered off and dried at RT. The sample prepared from TSD and TSM is labeled TSD-RS (standing for rod-shaped morphology) and TSM-IC (standing for isometric crystals), respectively.

The solid product was annealed in a muffle furnace for 1 hour at the temperature of 300, 500, 825, and 1200 °C. The heating was carried out in air atmosphere applying the heating rate of 5 °C min^{-1}. The sample was removed from the furnace after cooling down to the temperature of less than 40 °C.

Characterization of products

For morphological, structural, and chemical characterization of products the following methods were used: scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), precession electron diffraction tomography (PEDT), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, CHNS elemental analysis, thermogravimetry (TG), differential thermal analysis (DTA), and thermal analysis combined with mass spectrometry (TA/MS). Details including experimental conditions are described in Supporting Information – Characterization methods.

RESULTS AND DISSCUSION

Template-based methods of synthesis are often used for preparation of 1D titania structures[1, 10-12, 15, 22, 27-28]. Controlling the shape and size of the final TiO_2 particles thus converts into search for a suitable template. We observed that titanyl sulfate can serve as template for determining the size and shape of the prepared titania aggregates.

The crystals of titanyl sulfate (both monohydrate and dihydrate) when immersed in aqueous ammonia at temperature of about 0 °C provide solid residue composed of particles, whose shape and dimensions correspond perfectly to the particle morphology of the initial titanyl sulfate with composition matching to that of metatitanic acid, *i.e.* the products of the reaction form pseudomorphs of metatitanic acid after titanyl sulfate.

Pseudomorphs of metatitanic acid after titanyl sulfate

Particle shape of the two starting materials (TSD and TSM) is distinctly different (Figures 1 and 2). Sample TSD consists of regular rod–like crystals with the size of about 10-15 x 2 μm, whereas sample TSM is formed by aggregates of isometric crystals with broad size distribution. Both samples are rather chemically pure. According to the EDX analysis, both samples contain only Ti, S and O in ratios corresponding to the values expected from the chemical formula (hydrogen is not detectable by EDX spectroscopy). Neither sample contains any impurities in concentrations detectable by the EDX method (approx. ≥0.01 wt.%).

XRD patterns show that sample TSM corresponds to titanyl sulfate monohydrate ($TiOSO_4.H_2O$) with a known structure [29-30], while sample TSD consists of titanyl sulfate dihydrate ($TiOSO_4.2H_2O$) of which the structure has not been determined yet[26]. As a part of this study, we solved the structure of titanyl sulfate dihydrate using dynamical refinement of precession electron diffraction tomography data[31-33]. Details of the structure solution and refinement as well as description of both structures are presented in Supporting Information - Structure of hydrated titanyl sulfates.

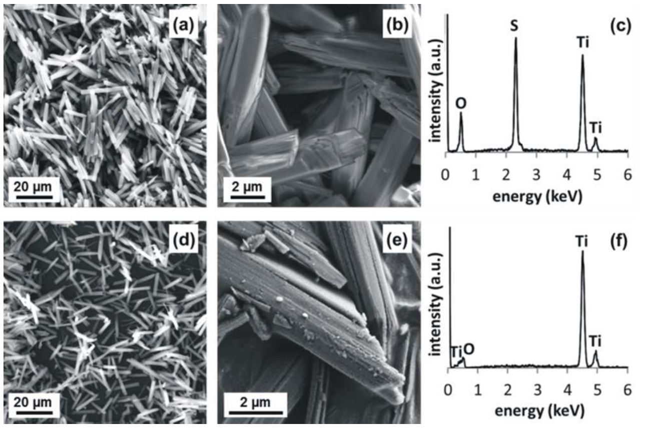

Figure 1. SEM observations of starting material TSD (a,b,c), and its product sample TSD-RS (d,e,f).

Immersing the rods of TSD into ice-cold concentrated aqueous ammonia, according to the above described synthetic procedure, results in the formation of rod-like particles with exactly the same size and shape as that of the starting material (Figure 1a,b,d,e). Behavior of TSM is similar (Figure 2a,b,d,e). Shape and size of the product particles remain the same as that of the starting TSM.

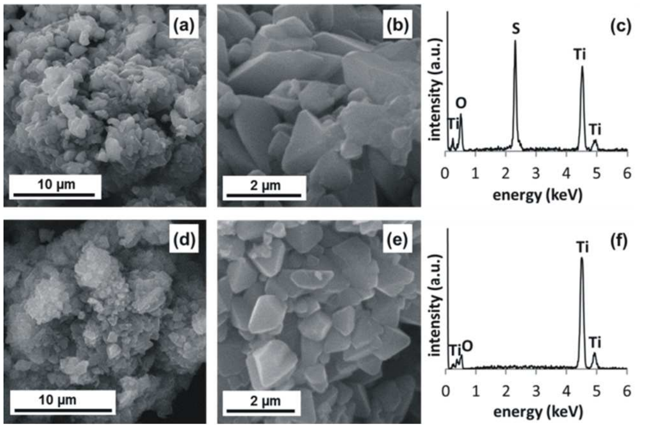

Figure 2. SEM observations of starting material TSM (a,b,c), and its product sample TSM-IC (d,e,f).

However, from the EDX spectra (Figures 1c,f and 2c,f), it is apparent that the products do not contain any sulfur, as corroborated by CHNS analysis (Table 1). The Ti/O ratio measured in the treated samples is about 1/3, whereas in the EDX analysis of the initial titanyl sulfate ($TiOSO_4$) the Ti/O ratio corresponds to 1/5. Ratio 1/3 is often found in various hydrated titania samples prepared from aqueous media, recently also from ammonia solutions[34-35]. This ratio is typical for variety titania materials such as hydrated titanium dioxide ($TiO_2.H_2O$) or materials named as metatitanic acid, H_2TiO_3 or $TiO(OH)_2$[36-38].

According to powder XRD, both TSD-RS and TSM-IC materials are amorphous (Figure S5).

TEM investigation (Figure 3) reveals that the morphology of particles of titanyl sulfate (sample TSD) is closely preserved in the resulting amorphous metatitanic acid (sample TSD-RS) including such details like the laminar structure (Figure 3a). The amorphous character of the material is documented by the corresponding electron diffraction pattern with only very broad signs of diffraction rings (Figure 3b), and by high-magnification image showing porous character of the product (Figure 3c). In case of the TSM-IC sample, the original compact isometric morphology is also preserved. Only particles without any fine structure were observed; even at the highest magnification the material looks completely smooth and homogenous (Figure S6).

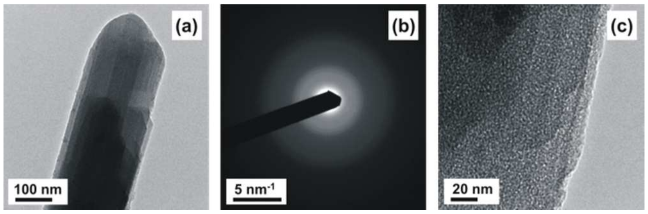

Figure 3. TEM observations of sample TSD-RS. (a) bright-field image, (b) selected-area electron diffraction, (c) high-resolution image.

The size and morphology of the initial TS particles is retained even after annealing up to 1200 °C as demonstrated on sample TSD-RS (Figure 4). The rod shape of the pseudomorphs is readily discernible, even though the phase composition changes from metatitanic acid through anatase to rutile (Supporting Information – Annealed sample of TSD-RS). The particles are polycrystalline, with the dimensions of the constituent crystals growing with annealing temperature.

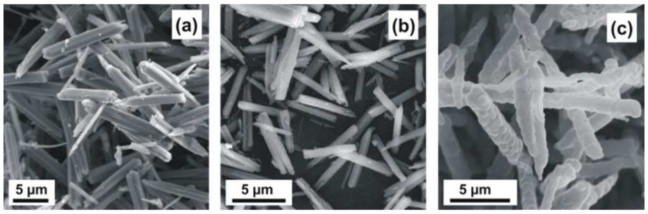

Figure 4. SEM observations of sample TSD-RS annealed at: (a) 500 °C, (b) 825 °C, (c) 1200 °C.

The FTIR spectra of both titanyl sulfate precursors as well as both products are very similar (Figure 5). The spectra of both precursors display an absorption band at 1226 cm^{-1} (TSM), 1220 cm^{-1} (TSD), correlating to sulfate group bonded to titanium, and several bands in the range from 990cm^{-1} to 1210 cm^{-1} corresponding to asymmetric sulfate bonding[39]. The presence of O-Ti-O-Ti vibrations is indicated by bands between 800 and 900 cm^{-1}. The presence of OH-groups is evidenced by characteristic bands at 3400 cm^{-1} and at 1600 cm^{-1}. The spectra of the prepared samples (TSD-RS and TSM-IC) do not display the bands characteristic for sulfates (900-1226 cm^{-1}). Both spectra indicate presence of NH_4^+ ions (bands at 3200 cm^{-1} and at 1400 cm^{-1}). The products also contain OH-groups (bands at 3400 cm^{-1} and at 1600 cm^{-1}). The band at 3400 cm^{-1} is more intense for TSD-RS than that of TSM-IC confirming higher amount of OH-groups in the sample TSD-RS. In both spectra of the products, bands at around 3400 cm^{-1} and 1630 cm^{-1} can be assigned to water physically adsorbed through hydrogen bridges, while the shoulders at 3150 cm^{-1} (TSM), and 3170/1436 cm^{-1} (TSD) correspond to more strongly bonded water[40-41]. In the low wavenumber region from 300 to 1000 cm^{-1}, a broad band is observed corresponding to Ti-O vibrations in octahedral (near 600 cm^{-1}) or tetrahedral (near 800 cm^{-1}) surroundings[42-44], and/or to stretching Ti-O-Ti vibrations in polytitanates[45]. The measured data are in good agreement with the FTIR data published earlier[46].

The Raman spectra confirm that the structure of pseudomorphs is completely different from the TS precursors (Figure 6). The Raman spectra of both products are very similar, despite the obvious difference between precursors, and can be related to the spectra of crystalline metatitanic acid[47]. However, our materials are amorphous, and therefore the observed Raman bands are broader. In the region from 100 to 300 cm^{-1}, intense wide bands of O-Ti-O bending vibrations are observed. Next, two double peaks at 409/ 451 cm^{-1} and 615/669 cm^{-1} are present, which can be both assigned to Ti-O stretching vibrations only to Ti-O bonds with a slightly different length. The splitting of the bands can be explained by breaking of the symmetry of TiO_6 octahedra, and consequent unequal strength of Ti-O bonds[47]. Due to the same reason, the band characteristic of O-Ti-O bending in metatitanic acid is also split with two maxima at 229 and 287 cm^{-1}, however the splitting is less pronounced than the one described in[47]. In the region 1300-1800 cm^{-1}, two bands are observed (1) at 1440 cm^{-1} of NH^{4+} vibrations[42], (2) at 1680 cm^{-1} of O-H-O bending. In the region from 2500 to 3700 cm^{-1}, bands caused by stretching vibrations of O-H and N-H bonds overlap strongly.

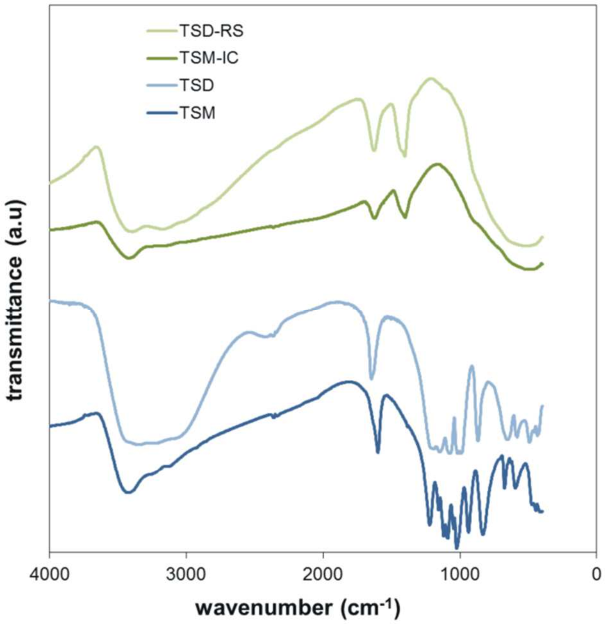

Figure 5. FTIR spectra of starting materials (TSM, TSD) and products (TSM-IC, TSD-RS).

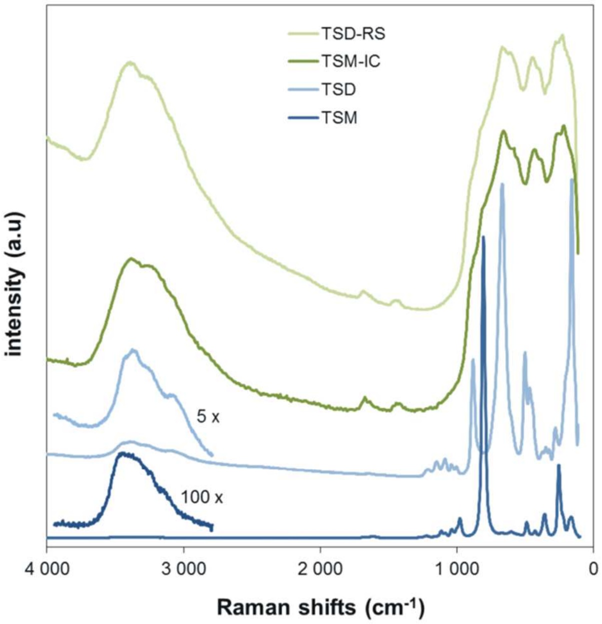

Figure 6. Raman spectra of starting materials (TSM, TSD) and products (TSM-IC, TSD-RS). Normalized spectra in the region from 100 to 1000 cm^{-1} (intensity of spectrum TSM, TSD enlarged by 100x, 5x, respectively).

According to the CHNS analysis (Table 1), the material contains significant amount of nitrogen (as NH_4^+) bound during the synthetic procedure, and lower amount of carbon (as CO_2) probably adsorbed from air after the process of preparation. Content of sulfur below 0.1 wt.% is in accordance with the EDX measurements. Presence of NH_4^+ ions confirmed by FTIR in both products indicates that prepared materials also contain negatively charged groups. With Ti/O ratio approaching 1/3 obtained from EDX analysis, it can be assumed that the amorphous reaction products correspond to metatitanic acid H_2TiO_3, rather than to hydrated titania $TiO_2.H_2O$. This acid is partially (by approx. 11 %) neutralized by NH_4^+. Moreover, as indicated by FTIR results (Figure 5), the prepared materials contain large amount of water; partly physically adsorbed on the large particle surface (Table 2), and partly bonded more strongly. TG analysis of TSD-RS[48] (Figure S11) shows two well-distinguished steps of water release: first step (30 - 130 °C) with the mass loss of 5-10 % (depending on heating rate) can be ascribed to physically adsorbed water, and second step (130 - 200 °C) corresponds to more strongly bonded water. Similar results were obtained for TSM-IC (Figure S11). From the above data we can conclude that the reaction products are formed of metatitanic acid, which is partially neutralized and hydrated. This can be expressed by general formula $(NH_4)_yH_{2-y}TiO_3 \, . \, xH_2O$; with the given data for TSD-RS $(NH_4)_{0.225}H_{1.775}TiO_3 \, . \, 0.593 \, H_2O$.

Table 1. CHNS analysis of TSD-RS and TSM-IC samples. Concentrations of NH_3, CO_2, H_2O, SO_3 and TiO_2 were calculated based on the total mass loss determined by thermogravimetric measurements.

Element	N	C	H	S	-
TSD-RS (wt.%)	2.8	0.3	3.6	< 0.01	-

TSM-IC (wt.%)	1.5	0.1	3.6	0.1	-
Compound	NH_3	CO_2	H_2O	SO_3	TiO_2
TSD-RS (mol.%)	7.6	0.8	58.1	0	33.5
TSM-IC (mol.%)	3.8	0.2	61.3	0.1	34.6

With the aim to investigate the influence of reaction conditions on the form of reaction products, the reaction on TSD was repeated with a variable volume of added concentrated ammonia (Table S5). In all but the lowest ammonia concentration, the substitution of sulfate ions by OH groups takes place, and morphologically identical rod-like amorphous pseudomorphs of metatitanic acid after TSD are formed. However, when the amount of used ammonia and pH of the solution is lowered, a product with lower content of NH_4^+ (Table S5) is obtained, which is still amorphous, but which is substantially less stable and tends to recrystallize to anatase. Even the exposure to electron beam during the TEM observation lead to the phase transformation to anatase within several minutes, whereas the product obtained at pH 9 needed annealing at 300 °C to get equally sensitive. The annealed material is still amorphous and a perfect pseudomorph (Figure S7a and S8a), but according to FTIR and Raman analyses contains no NH_4^+ and no adsorbed water. It can be concluded that the presence of relatively large NH_4^+ cations in the material is substantial for stabilizing its amorphous character, *i.e.* this cation hinders the linkage of Ti/O chains or octahedra into the anatase structure.

Surface area of both samples (Table 2) is quite high (about 300 $m^2 \cdot g^{-1}$) mostly due to the contribution of microporosity (Figure S9), also observed by TEM (Figure 3), which indicates possible significant reactivity of the materials. In comparison with sample TSM-IC, the sample TSD-RS has a higher total surface area by more than 40 $m^2 \cdot g^{-1}$. Also the pore volume of TSD-RS is slightly higher. On the other hand, the surface area of the starting materials (TSM and TSD) is lower than 1 $m^2 \cdot g^{-1}$, and therefore the porosity could not be evaluated.

Table 2. Results of the surface area and porosity measurements of TSD-RS and TSM-IC samples.

Sample	Micropore surface area ($m^2 \cdot g^{-1}$)	External surface area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Pore diameter (nm)
TSD-RS	317	27	0.18	0.45
TSM-IC	281	18	0.13	0.45

Sorption of radionuclides by metatitanic acid pseudomorphs

The unique shape of amorphous metatitanic acid pseudomorphs coupled with its high surface area and major contribution of microporosity predetermines its use as sorbent material. Recently, several papers have been published that demonstrate a significant adsorption capacity of metatitanic acid, particularly for lithium[49-51], and some heavy metals[52].It is also well known that the salts of metatitanic acid, *e.g.* sodium titanate, can be used as effective sorbent of radionuclides[53], or heavy metals[54].

The metatitanic acid pseudomorph TSD-RS was tested with success as a sorbent for radionuclide ^{85}Sr (Figure 7). The sorption was highly effective, Sr(II) uptake reaches 99 % for Sr(II) after 20 hours of contact time. Similar results were obtained for ^{134}Cs, for which the uptake reaches 90 %. The high capacity of metatitanic acid pseudomorphs significantly exceeds published data obtained with related materials[54].

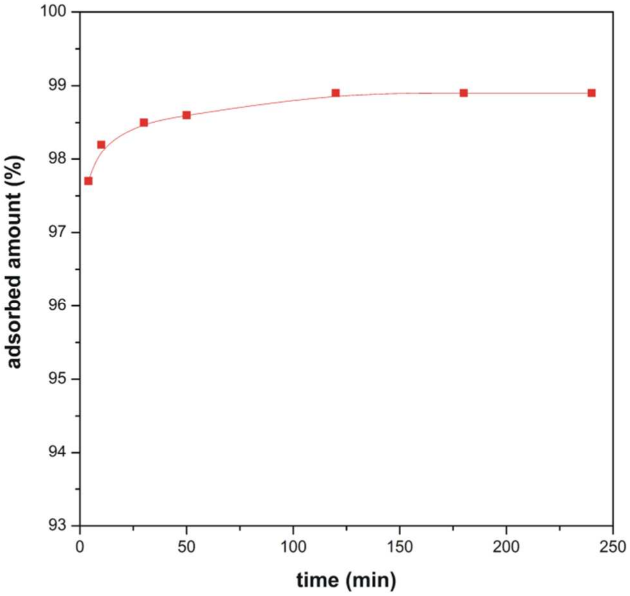

Figure 7. Sorption of ^{85}Sr by TSD-RS sample.

Formation mechanism of metatitanic acid pseudomorphs

The term pseudomorph defined as "a crystal consisting of one mineral but having the form of another" is a well-known phenomenon in mineralogy[55].

Formation of pseudomorphs after $TiOSO_4.2H_2O$ during chemical reaction has been previously reported. Facile release of water during thermolysis was observed for both $TiOSO_4.2H_2O$ and $TiOSO_4.H_2O$[56]. Complete dehydration of $TiOSO_4.2H_2O$ was reached at 225 °C. During the thermolysis, morphology of the $TiOSO_4.2H_2O$ particles is retained up to 950 °C, when anatase is transformed to rutile[57]. First, H_2O is gradually released accompanied by amorphization. Second, SO_3(g) is evolved at 540-580 °C accompanied by transformation to anatase. Such behavior is confirmed by TA-MS measurements of both TSM and TSD (Figure S11).

However, the behavior of TS under the reaction conditions described herein (presence of aqueous ammonia at 0 °C) is unexpected. Although the titanyl sulfate dihydrate is soluble in water within tens of minutes, the residue after the reaction with aqueous ammonia is not soluble in water; it is amorphous and it does not contain any sulfur. It can be assumed that in the concentrated ammonia the sulfate ions were extracted leaving the titania framework largely intact. To fully understand the unusual behavior of solid TS under the synthesis conditions described in this work is not easy. However, some guidance may be gained from the structures of TS.

The structure of titanyl sulfate monohydrate (TSM) is composed of two symmetry independent zig-zag chains of corner-sharing TiO_6 octhedra extending along **b** direction (Figure 8). The chains are interconnected by SO_4 tetrahedra into a 3D framework. The H_2O molecules point into the small channels extending along **b** direction.

The structure of titanyl sulfate dihydrate (TSD) is composed of two symmetry independent helices of corner sharing TiO_6 octahedra extending along **a** direction (Figure 9). Each pseudotrigonal helix is in addition held together by SO_4 tetrahedra that share corners with odd/even TiO_6 octahedra. The two H_2O molecules are attached to the remaining two oxygens of TiO_6 octahedron. Both hydrogens have H-bonds toward oxygens of two different SO_4 tetrahedra. One H-bond points to the oxygen of SO_4 tetrahedron from the same helix (intra-chain bond), while the other H-bond points to the oxygen of SO_4 tetrahedron from the neighboring helix (inter-chain bond). The whole 3D structure is therefore held together (in the **b** and **c** directions) by H-bonds only.

Naturally, the particle shape of TSD and TSM samples is determined by the atomic structure of the corresponding TS. 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 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. Although such structure cannot guarantee formation of polymorphs, it is a prerequisite for it. Given that during the reaction with the ammonia solution the morphology of the starting titanyl sulfate dihydrate is fully maintained, it can be assumed that during this reaction leaching of sulfate anions and their replacement with OH^- anions takes place.

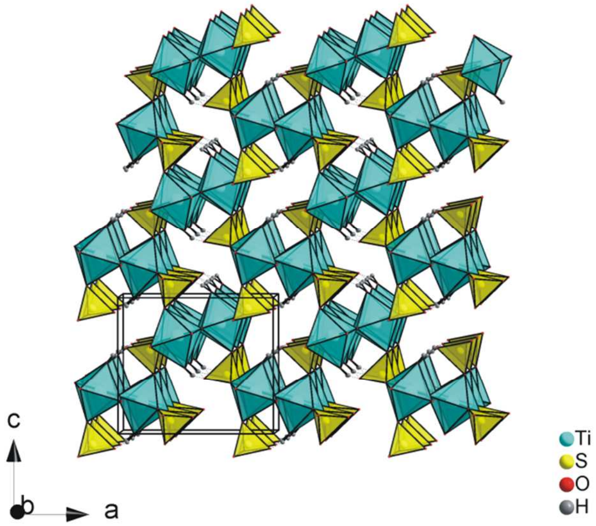

Figure 8. Structure of titanyl sulfate monohydrate (TSM).

The $(TiO_5)_n$ chains or helices are relatively strong against hydrating and dissolving in water, whereas sulfate anions located between these chains and helices are loosely bound, and under the reaction conditions readily pass into solution as $(SO_4)^{2-}$, while the $(TiO_5)_n$ chains, continuously extending through the whole crystal, remain intact during the substitution process and allow maintaining the original shape of the particles. The remaining $(TiO)^{2+}$ skeleton, according to its composition corresponding to amphoteric titanic acid H_2TiO_3, is partially neutralized by the base present in the solution producing an insoluble salt of amorphous titanic acid (NH_4TiO_3). Due to the amphoteric nature of the metatitanic acid, the cation content in the product is variable and depends on the final pH in the system. The whole process can be described by the following reaction (1).

$$TiOSO_4.2H_2O(s) + (2+y)\ NH_3(aq) \rightarrow (NH_4)_yH_{(2-y)}TiO_3.xH_2O(s) + (NH_4)_2SO_4(aq) \qquad (1)$$

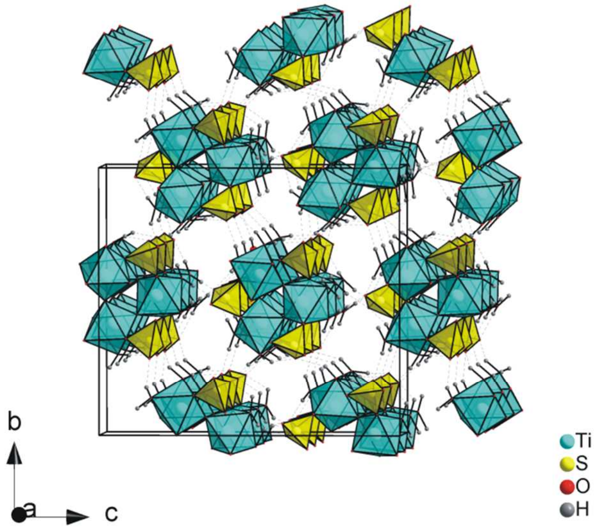

Figure 9. Structure of titanyl sulfate dihydrate (TSD).

From the structural point, the replacement of sulfate for OH^- anions does not cause a collapse of the structure as the newly bonded OH-groups repel one another. 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[47, 58-60].

The result of these reactions is the transformation of the originally highly water soluble titanyl sulfate into metatitanic acid insoluble in water while maintaining the particle shape and size of the original titanyl sulfate.

To corroborate the above described theory of formation mechanism of metatitanic acid pseudomorphs after hydrated titanyl sulfate, the solid products were sampled in 2-minute intervals during the synthesis, and their composition was analyzed by EDX spectroscopy (Figure 10). Samples prepared from titanyl sulfate dihydrate (TSD-RS) display much faster reaction rate compared to samples prepared from titanyl sulfate monohydrate (TSM-IC). Such behavior corresponds to a stronger 3D framework in TSM hindering the reaction progress. In addition, a dissolution experiment in distilled water was performed. TSD dissolved into pure transparent solution after 40 minutes, whereas TSM solution stayed cloudy even after 2.5 hours and heating at 35 °C.

Formation of pseudomorphs is characteristic only for titanyl sulfate due to its specific structural features. Hydrated vanadyl sulfate when subjected to the identical reaction conditions produced hydrolysis products whose morphological characteristics are unrelated to the shape of the particles of the starting salt (Figure S13). The structure of hydrated vanadyl sulfate is composed of isolated units of hydrated vanadium and sulfur polyhedra bound by H-bonds (Figure S12), which facilitate hydrolysis. The mechanism of hydrolysis in this case probably takes place simultaneously with the dissolution, and subsequent precipitation of the morphologically unrelated products. This further supports our description of the process based on the structure related mechanism of the pseudomorphs formation.

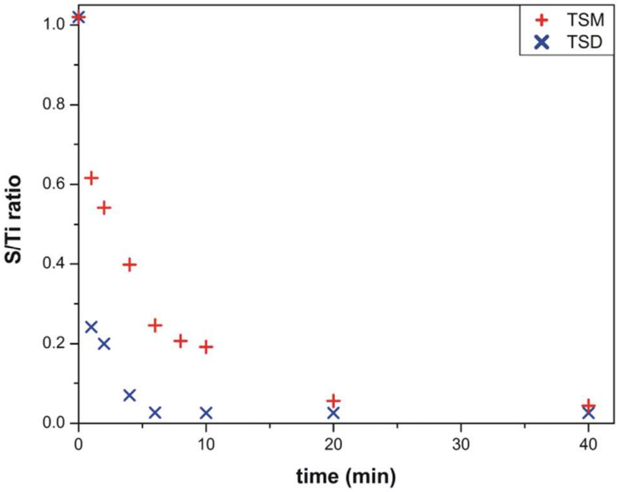

Figure 10. Rate of transformation of hydrated titanyl sulfates during the synthesis. The S/Ti ratio was determined from SEM/EDX analysis of at. % normalized.

CONCLUSIONS

Crystals of titanyl sulfate (both monohydrate and dihydrate) when immersed in aqueous ammonia at temperature of 0 °C provide solid residue particles whose shape and dimensions correspond perfectly to the particle morphology of the initial titanyl sulfate. The obtained material is amorphous and its chemical composition and other properties correspond to metatitanic acid partially neutralized with ammonia. 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. The individual particles are polycrystalline, while the dimensions of the constituent crystals grow with annealing temperature. The synthesized material is characteristic by high surface area combined with microporosity.

High porosity of the titanic acid and its ion exchange ability[61] to adsorb various anions or cations (demonstrated here on the sorption of Sr^{2+}) predetermine this material for water cleaning and similar applications as well as synthesis of various catalysts based on TiO_2. Owing to the high sorption capacity, the material can be also used for the synthesis of acicular titanate particles, like Li, Sr or Pb titanates.

The unique feature of the synthesized material is the close relationship between shape and size of the starting titanyl sulfate particles and morphology of particles of the prepared metatitanic acid. This fact allows preparing materials with the desired size and shape simply by controlling the particle shape over a wide range of the conditions of crystallization of the starting hydrated titanyl sulfate[26]. By annealing, polycrystalline anatase and rutile nanorods can be prepared. The described synthetic procedure opens new pathways for the synthesis of materials based on TiO_2 with controlled size and shape particles.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Characterization methods; Structure of hydrated titanyl sulfates; XRD of the products; TEM of TSM-IC; Annealed samples of TSD-RS; BET analysis; TA/MS of reactants and products; Synthesis - additional experiments; Hydrated vanadyl sulfate.

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Metatitanic acid pseudomorphs after titanyl sulfates: nanostructured sorbents and precursors for crystalline titania with desire particle size and shape

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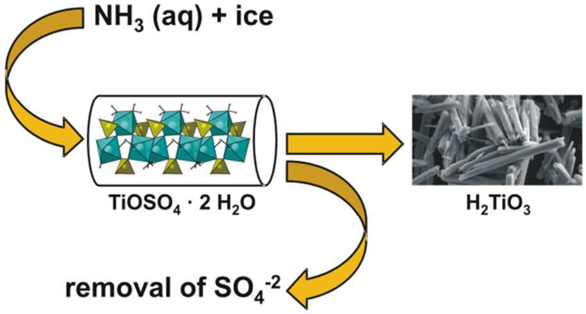

A new preparation method for the synthesis of TiO_2 microrods is based on the extraction of sulfate ions from the crystals of titanyl sulfate dihydrate in aqueous ammonia solution leaving the Ti-O framework intact. The resulting metatitanic acid possesses excellent sorption properties towards radionuclides, and transforms to TiO_2 upon heating. The morphology of particles remains unchanged during the whole process.