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New hierarchical titania-based structures for photocatalysis

Ivan A. Kovalev,[a] Andrey A. Petrov,[b] Olga A. Ibragimova,[b] Alexander V. Shokod’ko,[a] Andrey S. Chernyavskii,[a] Eugene A. Goodilin,[b,c] Konstantin A. Solntsev[a,b] and Alexey B. Tarasov*[a,b]

[a] *A. A. Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: alexey.bor.tarasov@gmail.com*
[b] *Department of Materials Science, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[c] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

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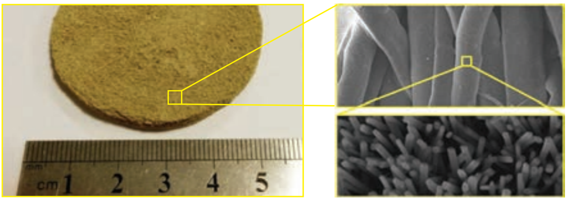
A new preparation method of bulk hierarchic titania structures for photocatalysis is proposed. A highly porous metallic Ti preform was converted into TiO_2 for the first time using a combination of an oxidative construction of thin-wall ceramics (OCTWC) method, intermediate transformation into sodium titanate by hydrothermal treatment in alkaline aqueous solutions and shape preserving removal of sodium by a secondary hydrothermal treatment in acidic aqueous solution yielding a material of rutile/anatase titania with highly developed surface and high photocatalytic activity.



Photocatalytic decomposition of contaminants under ultraviolet irradiation is promising for water and air purification.[1–5] In particular, titanium dioxide is of interest as a promising nanomaterial for photocatalysis due to its low cost, availability, stability, and high functional characteristics.[6,7] In the course of air purification, photocatalysis is very efficient when it is coupled with electrofiltration. The latter removes dust and significantly reduces the load on the photocatalytic filter. However, a drawback of electrofiltration is that an increase in power may lead to the formation of ozone, which is a good oxidizer but toxic for humans in high concentrations. It was shown that photocatalytic oxidation can also be used to decompose ozone;[8–10] therefore, the development of combined systems based on an electrostatic filter with a photocatalytic cell is of considerable current interest. In this case, bulky materials with highly developed surface are needed, which can either perform photocatalysis or act as an effective substrate for photocatalysts.[11–13]

Highly porous TiO_2 can be obtained by an innovative process of the oxidative construction of thin-wall ceramics (OCTWC), which is based on the controlled high-temperature oxidation of metallic preforms with any design to the oxides that preserve the initial shape and dimensions of the metallic precursor.[14] However, only the most thermodynamically stable oxides in higher oxidation states are formed in this process. As a result, titanium can be only oxidized into a photocatalytically inactive rutile phase.

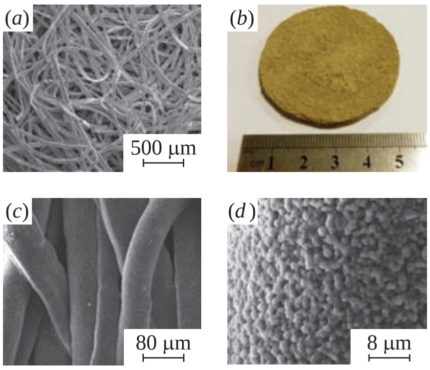


Figure 1 Titanium felt (*a*) before and (*b*–*d*) after the OCTWC process.

Recently, a novel approach has been proposed to transform rutile nanoparticles into an anatase phase through a hydrothermally processed intermediate protonated form of sodium titanate.[15] Herein, we combined the OCTWC approach with the subsequent two-step hydrothermal treatment in order to obtain a bulk material with a highly developed surface area and high photocatalytic performance.

At the initial stage, we optimized the temperature of titanium oxidation. Titanium foils with a 300 μm thickness were oxidized in an oven at temperatures of 700–1100 °C from 2 to 144 h in air. The optimal temperature was 875 °C, as a lower temperature significantly decreased the rate of the reaction while the higher temperatures resulted in rapid oxidation leading to the high thickness deviation of the resulting material. It was found that the oxidation was complete in 72 h with no changes in the morphology and phase composition at longer synthesis times. Using these synthesis conditions, we successfully converted titanium felt into rutile [Figures 1, 2(*a*)].

We applied hydrotermal treatment to the obtained material to result in a photocatalytically active anatase phase with well-developed surface. The described two-step hydrothermal treatment method was previously applied to titania nanoparticles.[15]

The first hydrothermal treatment of rutile felt was performed in strongly alkaline aqueous solution (15 M NaOH) at 200 °C for 48 h. During the process, the nanorods of sodium titanates 300–500 nm in diameter grew on the surface of rutile [Figures 2(*b*), 3(*a*),(*b*)] according to the reactions

$$3\,TiO_2(\text{rutile}) + 4\,NaOH \rightarrow Na_4Ti_3O_8 + 2\,H_2O \text{ and}$$

$$3\,TiO_2(\text{rutile}) + 2\,NaOH \rightarrow Na_2Ti_3O_7 + H_2O.$$

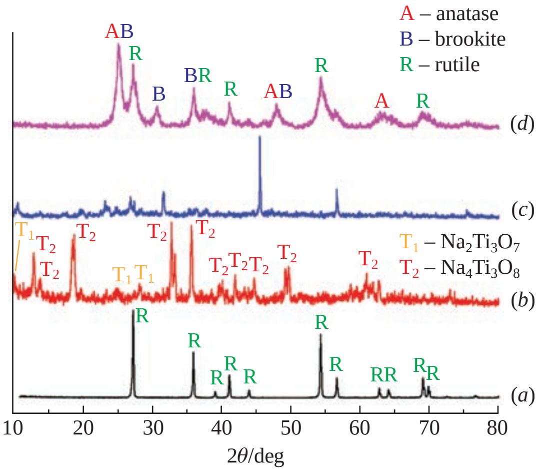


Figure 2 (*a*) Rutile felt, (*b*) sodium titanates $Na_4Ti_3O_8 + Na_2Ti_3O_7$, (*c*) protonated form of sodium titanates, and (*d*) anatase + brookite on the rutile felt.

Then, the rutile felt functionalized with sodium titanates was washed in a 2.5 M solution of HCl to obtain the protonated forms of sodium titanates, although the precise phase identification using powder diffraction is complicated due to the formation of an uncertain mixture of several intermediate titanates [Figure 2(*c*)].[16] After that, the second hydrothermal treatment was applied to synthesize anatase from the protonated sodium titanates. The synthesis was carried out in a 0.05 M aqueous solution of HNO_3 at 120 °C for 48 h. The obtained material was washed with distilled water and dried. Scanning electron microscopy showed that the nanorods inherited the morphology of sodium titanate and further increased the surface area [Figure 3(*c*),(*d*)], whereas powder X-ray diffraction analysis revealed that the nanorods were made of anatase with an admixture of brookite, which is also photocatalytically active[17] [Figure 2(*d*)]. The diffraction pattern of the final material showed rutile reflections from the original bulk rutile fibers underlying the nanorods, while the presence of a brookite phase together with anatase can be explained by the size effect, which leads to the stabilization of either brookite or anatase phases depending on their particle sizes [Figure 3(*d*)].[18]

The specific surface areas of anatase nanorods grown on the surface of rutile felt obtained by single-point and multipoint BET methods were S_d = 50 m^2 g^{-1}, which is much higher than the specific surface area of the initial rutile phase (1–3 m^2 g^{-1}).

The photocatalytic activity of the material obtained was measured in the course of an ozone decomposition reaction. Ozone was supplied through a purge cell with a filter made of a test material (rutile felt or rutile felt functionalized with anatase). Commercially available Degussa P-25 TiO_2 powder deposited on porous quartz was used for comparison. The drop in ozone concentration was detected after passing through an illuminated photocatalytic cell. A UV lamp (6 W) with a wavelength of 254 nm was used for illumination; ozone was generated using an OPTEK GS-024-25 system (flow rate through a cell, 2 dm^3 min^{-1}) and was analyzed on an OPTEK 3.02P-R analyzer.

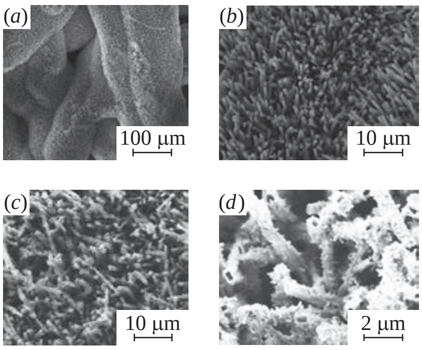


Figure 3 (*a*), (*b*) Nanorods of sodium titanate $Na_4Ti_3O_8$ on the surface of rutile felt and (*c*), (*d*) the nanorods of anatase.

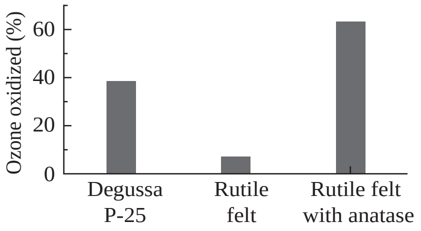


Figure 4 Photocatalytic activity of tested titania materials.

The concentration of ozone dropped down by 7% if the rutile felt was used as a photocatalytic filter, while a filter made of the rutile felt functionalized with anatase showed a drop in the concentration of ozone by 63%. The latter is higher by a factor of almost 1.7 than that in the case of the well-known Degussa P-25 TiO_2 powder, which demonstrated only a 38% decrease in ozone concentration.

Thus, we applied for the first time an approach to the oxidative construction of thin-wall ceramics with the subsequent hydrothermal treatment and obtained a bulk hierarchical multiscalable anatase material for photocatalysis with a surface area of 50 m^2 g^{-1}. At the first stage, we converted titanium fest into rutile. Further hydrothermal treatment led to the formation of sodium titanate nanorods, which were subsequently transformed into a protonated form and, finally, into anatase. We demonstrated that the proposed method allows one to create bulk rutile structures modified with anatase with a well-developed surface and high photocatalytic activity comparable with that of industrially applied titania powders.

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