Materials Research Bulletin 49 (2014) 405–412

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Highly photoactive 2D titanium dioxide nanostructures prepared from lyophilized aqueous colloids of peroxo-polytitanic acid

Jan Šubrt *, Petra Pulišová, Jaroslav Boháček, Petr Bezdička, Eva Pližingrová, Lenka Volfová, Jaroslav Kupčík

Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 25068 Řež, Czech Republic

ARTICLE INFO

Article history:
Received 22 April 2013
Received in revised form 4 September 2013
Accepted 17 September 2013
Available online 24 September 2013

Keywords:
A. Oxides
A. Layered compounds
C. Electron microscopy
C. Raman spectroscopy
C. X-ray diffraction

ABSTRACT

Reaction of hydrogen peroxide with suspensions of thoroughly washed precipitates obtained by neutralization of aqueous solution of titanyl sulfate with aqueous ammonia leads to transparent yellow liquids. In this way prepared colloid solution is a two phase system in which, beyond the water phase, also a liquid hydrated peroxo-polytitanic acid component is present. Freeze drying of this colloid liquid provides a foamy material consisting of thin foils of peroxo-polytitanic acid containing small but not negligible amount of chemically bound ammonia. These foams annealed at temperature above ~200 °C lose water, ammonia and excess of oxygen providing foamy amorphous oxide. At higher temperatures above ~280 °C the amorphous material crystallizes to anatase which transforms at temperatures >850 °C to rutile. The size and shape of the initial leaflets forming the foam is preserved up to ~900 °C. Slit shaped porosity is formed during annealing. We observed that the annealed material is highly photoactive, probably owing to highly anisotropic shape of anatase aggregates and their perfect crystallinity.

1. Introduction

Titanium dioxide attracted a great attention since Fujishima and Honda [1] discovered in 1972 the photocatalytic splitting of water on TiO_2 electrode. In the last decades, the application of nanosized TiO_2 focused on environmental remediation, especially water and air cleaning commanded attention to this phenomenon. TiO_2 is an efficient photocatalyst, properties of which depend crucially on size and shape of nanoparticles forming the material [2–10]. Because of high efficiency, high photostability, low cost, and nontoxic qualities, titania-based photocatalysts are still the most extensively studied materials for the photocatalytic production of hydrogen from water and remediation of polluted environment. The effects of the chemical and physical properties of titania, including crystal phase, crystallinity, particle size, and surface area, on its photoactivity have been identified by many investigations [3,11], however, the quantum yields achieved are still too low for many industrial applications.

Semiconductor-mediated heterogeneous photocatalysis is a promising technology for air and water cleaning without generating harmful by-products. The photocatalyst with designed physicochemical properties is the key in the process. Utilization of particulate photocatalysts will create some technological problems, such as difficulty in recycling and management. Thus, cost-effective methods for mass production of highly active photocatalysts that can be operated in an industrial photoreactor with less energy consumption and harmless subsequent consequences are increasingly attracting research attention. Photocatalysts with controllable morphologies at a wide range of scales shall be taken into account in designing the photocatalyst [5].

Titania foam is considered as a shape of nanostructured TiO_2 offering good prospects for industrial application. It is typical by low apparent density, high porosity and high sorption ability which results in high photocatalytic activity [12–17]. Titania foams could combine high photocatalytic activity with sorption ability for various organic materials and could be promising for environmental purification processes. Syntheses of titania foams are mainly based on use of surfactants and various templates [12,13,17–19] or bubbling gas through a mixture of a surfactant and a sol–gel precursor [14]. Formation of titania layers on surface of foams based on various materials like glass [15], ceramics [16,19–23] or metals [21] was also used to synthesize foamy TiO_2.

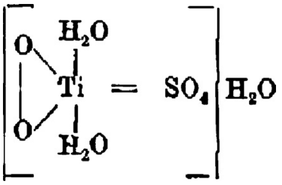
It is well known that Ti(IV) salts dissolved in water form stable transparent yellow solutions with hydrogen peroxide which slowly decompose under release of oxygen within the range of days [24]. It was demonstrated that the ratio of Ti:O (peroxy) is

---

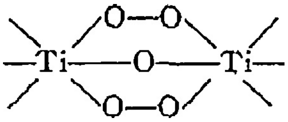
* Corresponding author. Tel.: +420 723899646.
E-mail addresses: subrt@iic.cas.cz, jan.subrt@post.cz (J. Šubrt).

0025-5408/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2013.09.028

commonly not 1:1, even in the freshly prepared complexes, in the solid state being usually 1:0.65 as an maximum value in the light yellow hydrated titanyl peroxide [24,25]. Patel and Mohan [25] suggest structure (1) for Ti(IV) peroxo complexes.


(1)

Muhlebach et al. showed [26] that the strongly colored 1:1 adducts formed from Ti-(IV) and H_2O_2 are binuclear. Their experiments show that peroxotitanium is present in very acidic solutions as a cation with a single charge per metal. The complex is probably mononuclear TiO_2OH^+ below pH 1, but condenses to a dinuclear species at least between pH 1 and 3, the unit Ti_2O_5 appears to be especially stable. The presence of groups $Ti_2(O_2)_2O.aq^{2+}$ is expected, it was suggested that the metal atoms are bridged by a μ-oxygen and two μ-peroxy groups. This leads to the postulated structure, the sixfold coordination being completed by H_2O or the ligand atoms of a chelating agent. Assuming regular octahedra, a Ti–O distance of 1.94 Å, and an O–O distance between 1.32 and 1.488 Å, this would be a remarkably strain-free complex with a Ti–O–Ti angle between 103° and 107°. It requires the grouping Ti–O–O–Ti to be planar (see structure (2)) [26,27].


(2)

Polymerization of the mentioned complexes at higher concentrations of Ti(IV) and higher pH values in aqueous media can lead to formation of stable yellow sols. It was observed that as the solution aged, the pH rose and the color changed from orange to yellow, eventually leading to the formation of transparent gels [28]. Such yellow colloids were used e.g. for preparation of TiO_2 layers on various substrates [29].

When the yellow colloid solution is dried on air at room temperature, a compact glassy yellow substance is formed which can be in no manner resuspended again in water. We observed at the beginning of our studies that the yellow peroxo-polytitanic acid substance can be completely separated out of the colloid solution of Ti(IV) peroxides prepared according to the described procedure by filtration using filters with relatively big pore size (few μm) leaving white filtrate, although the initial yellow solution was quite transparent and the expected very small nanoparticles should come through the filter. This observation indicated that the peroxo-polytitanic acid colloids in water form a separate probably liquid phase. In several papers the peroxo-polytitanic acid precursors were used for synthesis of anatase nanoparticles by hydrothermal treatment [30–33]. This method leads to remarkably uniform photoactive anatase nanoparticles.

Freeze-drying has been considered as a good technique to prepare long-term stable colloidal nanoparticles preserving utmost the situation in the initial aqueous system. It was demonstrated that the freeze-dried products possess many desirable characteristics, like the preservation of the primary physical and chemical characteristics of the product, short reconstitution time, low or unmodified particle size distribution, and acceptable relative humidity, and long-term stability [34,35].

The main idea of this study was based on the assumption that freeze drying – a method able to remove the aqueous component by sublimation at low temperature – will preserve the structure of the gelatinous part of the colloid also in dry state. We expected formation of foamy material with properties unusual to products prepared using any other synthetic method.

2. Experimental

2.1. Chemicals

Following chemical were used for syntheses: 29% aqueous ammonia; hydrogen peroxide of analytical grade purity, solution purum p.a., ≥30%; and Titanium(IV) oxysulfate ≥29% Ti (as TiO_2) basis, technical grade purity provided by Sigma Aldrich. Deionized water with conductivity 0.055 μS was used as reaction medium.

2.2. Sample preparation

We prepared the freeze dried titania foams from the peroxo-polytitanic acid gel according to following procedure (see scheme in Fig. 1). 4.80 g of titanyl sulfate was dissolved in 150 mL of water and cooled to 0 °C under stirring at 35 °C, until full dissolution of the salt and clarification the solution was reached. The solution was then precipitated by dropwise addition of concentrated aqueous NH_3 into the solution until pH 8 was reached, the temperature of the solution increased from 0 °C to approx. 7 °C. The white precipitate formed was filtered off, washed, and transferred into a beaker and re-suspended in 350 mL of deionized water. Then 26 mL of 30% aqueous H_2O_2 was added to the suspension. After addition of H_2O_2, the color of the white suspension turns to yellow and the pH decreased to 1–2. The suspension was then stirred at approx. 23 °C for 10–90 min until clear transparent yellow solution formed. The solution was sprayed into liquid N_2, the frozen material was transferred into freeze dryer (VirTis Benchtop K, Cole Parmer UK) and lyophilized at temperature of the condenser −64 °C and pressure 5–10 mtorr until full removal of ice. The dried peroxo-polytitanic acid occurred in form of yellow foam consisting of thin foils and was amorphous to X-rays, its apparent density was only ~1–10 g/dm^3, depending on the concentration of the initial peroxo-polytitanic acid colloid. Scheme of the synthesis is given in Fig. 1. Part of the yellow liquid was left to evaporate freely in a baker on air at laboratory temperature for two weeks. After this time, the clear yellow liquid turned to yellow glassy material.

The lyophilized material can be transformed easily into anatase by annealing. Annealing has been carried out in air, heating rate used was 5 °C min^{-1}, after reaching the required value the temperature was maintained constant for 2 h. The results of thermoanalytical study of the peroxo-polytitanic acid foam were published earlier [36].

2.3. Chemical analysis

Manganometric method [37] was used for determination of peroxide content in the solid sample. The following reaction occurs when potassium permanganate solution is added to hydrogen peroxide solution acidified with dilute sulfuric acid:

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{2+} + 5O_2 + 8H_2O \qquad (2)$$

This equation forms the basis of the method of analysis given below.

The content of Ti was determined using the semiquantitative EDS analysis method (estimated error of the determination is ±5%).

The content of ammonia was determined by using the instrument Elementar vario EL III produced by Elementar Analysensysteme GmbH, Donaustraße 7, 63452 Hanau (Germany). The determination error of C, H, N, and S determination guaranteed by the producer should be better than <0.1% abs. for each element.