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Highly photoactive anatase foams prepared from lyophilized aqueous colloids of peroxo-polytitanic acid

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ABSTRACT

Peroxo-polytitanic acid foams annealed at temperature above 500 °C lose volatile components and excess of oxygen providing anatase in the form of thin leaves consisting of intergrown nanocrystalline anatase particles which transform at temperatures above 850 °C to rutile. The size and shape of the initial leaflets forming the foam is preserved up to ~900 °C. We observed that the annealed material is highly photoactive, owing to highly anisotropic shape of anatase aggregates and their perfect crystallinity. Outstanding photocatalytic activity determined by measuring the kinetics of degradation of Methylene Blue (MB) and 4-chlorphenol (4-CP) as well as measuring the formation of hydroxyl radical spin adducts by EPR spectroscopy was observed. All three methods demonstrated significantly higher activity in comparison with the Degussa P25 photocatalyst. Both methods used for photoactivity tests provided similar results, the activity increased with increasing annealing temperature in order 500 °C < Degussa P25 < 600 °C < 850–950 °C. Results of measurement of formation of •OH radicals by EPR also confirmed the unusually high activity of our materials. In comparison with the Degussa P25, the sample annealed at 950 °C showed significantly higher production of •OH radicals.

1. Introduction

Among the advanced oxidation processes the semiconductor photocatalysis plays still a very important role in waste water and air cleaning. Improvement of the photocatalytic activity of TiO_2 is necessary in order to implement photocatalysis in real-life applications. Development of modified types of photocatalysts characterized not only by improved photoactivity but also possessing other properties, important from the point of view of particular technological application, is the key condition of more widespread utilization of this promising technology [1–6].

It is generally accepted that shape and size of photocatalyst particles belongs among the key factors determining not only the photocatalytic performance of any photocatalyst but also its applicability in real technological processes [5]. 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 [7].

It is well known that determination of photocatalytic activity is a very complicated task because of complex nature of the processes participating in reactions used for the activity evaluation. Because formation of the •OH radicals always participates in these reactions, direct measurement of this phenomenon, e.g., using EPR, can help with realistic evaluation of photoactivity of particular photocatalysts [8,9]. Similarly, determination of photocatalyst activity using measurement of kinetics of photocatalytic decomposition of various model chemicals depends significantly on the conditions used. Therefore, use of standard methods for testing the photoactivity is crucial for real determination of performance of particular photocatalyst [10,11].

Titania foam is considered as a form of nanostructured TiO_2 which offers good prospects for industrial application. It is typically characterized by low apparent density, high porosity, and high sorption ability, which results in high photocatalytic activity [12]. Titania foams could combine high photocatalytic activity

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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 [12–15] or bubbling gas through a mixture of a surfactant and a sol–gel precursor [16]. Formation of titania layers on surface of foams based on various materials like glass [17], etc. was also used to synthesize foamy TiO_2.

It is well known that Ti^{4+} salts dissolved in water form stable transparent yellow solutions with hydrogen peroxide which slowly decompose under release of oxygen within the range of days. It was demonstrated that the ratio of Ti:O (peroxy) is commonly not 1:1, even in the freshly prepared complexes, in the solid state being usually 1:0.65 as a maximum value in the light yellow hydrated titanyl peroxide [18,19]. Polymerization of the mentioned complexes at higher concentrations of Ti^{4+} 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. Such yellow colloids were used, e.g., for preparation of TiO_2 layers on various substrates [20] as well as sols of remarkably uniform shaped anatase nanoparticles [21–24]. It is well known 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 colloids also in dry state [25,26]. We expected that lyophilization of peroxo-polytitanic acid gels will lead to formation of highly porous material with properties unusual to products prepared using any other synthetic method.

In our recent publications [27,28] we studied the reaction of hydrogen peroxide with suspensions of thoroughly washed precipitates obtained by neutralization of aqueous solution of titanium oxysulfate with aqueous ammonia leading 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 [27]. We observed that 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 to rutile at temperatures above 850 °C. 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 [27,28].

2. Materials and methods

2.1. Chemicals

Aqueous ammonia (25%), hydrogen peroxide aqueous (30%), sulfuric acid (96%) and titanium oxysulfate ($TiOSO_4{\cdot}H_2O$) (all Sigma–Aldrich), as well as hydrochloric acid (LachNer, Czech Republic) were used as received. The spin trap 5,5-dimethyl-1-pyrroline N-oxide (DMPO, Sigma–Aldrich) was distilled before application. 4-Chlorophenol (Sigma–Aldrich) with purity ≥ 99% and Methylene Blue (Riedel-de Haën), purity 96% were used for determination of photoactivity.

2.2. Sample preparation

We prepared the freeze dried titania foams from the peroxo-polytitanic acid gel according to the procedure described in our recent publication [27]. 4.80 g of titanium oxysulfate was dissolved in 150 mL of water under stirring at 35 °C, until full dissolution of the salt and clarification of the solution was reached, then it was let cool down to 0 °C. 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 formed white precipitate 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 turned 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 a freeze dryer and lyophilized at temperature of the condenser −64 °C and pressure 5–10 mTorr until full removal of water ice.

This procedure led to yellow foamy cryogel. Macroscopically, the lyophilized samples looks like light brittle yellow foam (apparent density 2–10 g L^{-1}) composed of thin foils of dry gel, the properties of which depend on the method used for freezing the material. From the specific surface area about 150 m^2/g results that the foils should be very thin, in the order of tens of nanometers. The dried peroxytitanate occurred in the 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 peroxotitanate colloid.

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 peroxotitanic acid foam were also published earlier [28]. Samples were annealed at 500, 650, 800, and 950 °C, and are labeled accordingly as TIG-500, TIG-650, TIG-800, and TIG-950.

2.3. Structure and morphology characterization

Morphology of the deposits and EDS chemical analysis was studied by scanning electron microscopy (SEM). A Philips XL30 CP microscope (W-cathode, 20 nm resolution at 1 kV) was used for initial observation. For high-resolution imaging a field emission scanning electron microscope (FE-SEM) JEOL 7500F was used (resolution 1.4 nm at 1 kV).

Detailed phase analysis including imaging, electron diffraction and elemental analysis was carried out on a high-resolution transmission electron microscope (HRTEM) JEOL JEM 3010 microscope equipped with an EDS detector Oxford Instruments INCA Energy operated at 300 kV (LaB_6, cathode, point resolution 1.7 Å). Images were recorded on a Gatan CCD camera with resolution 1024 × 1024 pixels using the Digital Micrograph software package. The powder was dispersed in ethanol and the suspension was treated in ultrasound for 2 min. A drop of very dilute suspension was placed on a holey-carbon coated Cu-grid and allowed to dry by evaporation at ambient temperature.

Particle size was determined from TEM micrographs. In the first step, particle size area was measured in ImageJ, and this data were transferred to MS Excel. In the second step, histogram of particle size area was plotted, and subsequently weighted average and particle size was calculated.

2.4. Determination of photocatalytic activity

For assessing the photocatalyst activity we used two chemically different methods, namely degradation of Methylene Blue (MB) [10] and decomposition of 4-chlorophenol (4-CP) [29]. Both methods are widely used for determination of activity of various photocatalysts. As the standard photocatalyst, activity of